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Preface Thermodynamics

Welcome to *University Physics*, an OpenStax resource. This textbook was written to increase student access to high-quality learning materials, maintaining highest standards of academic rigor at little to no cost.

About OpenStax

OpenStax is a nonprofit based at Rice University, and it's our mission to improve student access to education. Our first openly licensed college textbook was published in 2012 and our library has since scaled to over 20 books used by hundreds of thousands of students across the globe. Our adaptive learning technology, designed to improve learning outcomes through personalized educational paths, is currently being piloted for K–12 and college. The OpenStax mission is made possible through the generous support of philanthropic foundations. Through these partnerships and with the help of additional low-cost resources from our OpenStax partners, OpenStax is breaking down the most common barriers to learning and empowering students and instructors to succeed.

About *University Physics*

Coverage and Scope

Unit 1: Thermodynamics

Chapter 1: Temperature and Heat

Chapter 2: The Kinetic Theory of Gases

Chapter 3: The First Law of Thermodynamics

Chapter 4: The Second Law of Thermodynamics

Pedagogical Foundation

Throughout *University Physics* you will find derivations of concepts that present classical ideas and techniques, as well as modern applications and

methods. Most chapters start with observations or experiments that place the material in a context of physical experience. Presentations and explanations rely on years of classroom experience on the part of long-time physics professors, striving for a balance of clarity and rigor that has proven successful with their students. Throughout the text, links enable students to review earlier material and then return to the present discussion, reinforcing connections between topics. Key historical figures and experiments are discussed in the main text (rather than in boxes or sidebars), maintaining a focus on the development of physical intuition. Key ideas, definitions, and equations are highlighted in the text and listed in summary form at the end of each chapter. Examples and chapter-opening images often include contemporary applications from daily life or modern science and engineering that students can relate to, from smart phones to the internet to GPS devices.

Assessments That Reinforce Key Concepts

In-chapter **Examples** generally follow a three-part format of Strategy, Solution, and Significance to emphasize how to approach a problem, how to work with the equations, and how to check and generalize the result. Examples are often followed by **Check Your Understanding** questions and answers to help reinforce for students the important ideas of the examples. **Problem-Solving Strategies** in each chapter break down methods of approaching various types of problems into steps students can follow for guidance. The book also includes exercises at the end of each chapter so students can practice what they've learned.

Conceptual questions do not require calculation but test student learning of the key concepts.

Problems categorized by section test student problem-solving skills and the ability to apply ideas to practical situations.

Additional Problems apply knowledge across the chapter, forcing students to identify what concepts and equations are appropriate for solving given problems. Randomly located throughout the problems are **Unreasonable Results** exercises that ask students to evaluate the

answer to a problem and explain why it is not reasonable and what assumptions made might not be correct.

Challenge Problems extend text ideas to interesting but difficult situations.

Answers for selected exercises are available in an **Answer Key** at the end of the book.

About the Authors

Senior Contributing Authors

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Dr. Samuel Ling has taught introductory and advanced physics for over 25 years at Truman State University, where he is currently Professor of Physics and the Department Chair. Dr. Ling has two PhDs from Boston University, one in Chemistry and the other in Physics, and he was a Research Fellow at the Indian Institute of Science, Bangalore, before joining Truman. Dr. Ling is also an author of *A First Course in Vibrations and Waves*, published by Oxford University Press. Dr. Ling has considerable experience with research in Physics Education and has published research on collaborative learning methods in physics teaching. He was awarded a Truman Fellow and a Jepson fellow in recognition of his innovative teaching methods. Dr. Ling's research publications have spanned Cosmology, Solid State Physics, and Nonlinear Optics.

Jeff Sanny, Loyola Marymount University

Dr. Jeff Sanny earned a BS in Physics from Harvey Mudd College in 1974 and a PhD in Solid State Physics from the University of California–Los Angeles in 1980. He joined the faculty at Loyola Marymount University in the fall of 1980. During his tenure, he has served as department Chair as well as Associate Dean. Dr. Sanny enjoys teaching introductory physics in particular. He is also passionate about providing students with research experience and has directed an active undergraduate student research group in space physics for many years.

Bill Moebs, PhD

Dr. William Moebs earned a BS and PhD (1959 and 1965) from the University of Michigan. He then joined their staff as a Research Associate for one year, where he continued his doctoral research in particle physics. In 1966, he accepted an appointment to the Physics Department of Indiana Purdue Fort Wayne (IPFW), where he served as Department Chair from 1971 to 1979. In 1979, he moved to Loyola Marymount University (LMU), where he served as Chair of the Physics Department from 1979 to 1986. He retired from LMU in 2000. He has published research in particle physics, chemical kinetics, cell division, atomic physics, and physics teaching.

Introduction

class="introduction"

These snowshoers on Mount Hood in Oregon are enjoying the heat flow and light caused by high temperature. All three mechanisms of heat transfer are relevant to this picture. The heat flowing out of the fire also turns the solid snow to liquid water and vapor. (credit: modification of work by “Mt. Hood Territory”/Flickr)



Heat and temperature are important concepts for each of us, every day. How we dress in the morning depends on whether the day is hot or cold, and most of what we do requires energy that ultimately comes from the Sun. The study of heat and temperature is part of an area of physics known as thermodynamics. The laws of thermodynamics govern the flow of energy throughout the universe. They are studied in all areas of science and engineering, from chemistry to biology to environmental science.

In this chapter, we explore heat and temperature. It is not always easy to distinguish these terms. Heat is the flow of energy from one object to another. This flow of energy is caused by a difference in temperature. The transfer of heat can change temperature, as can work, another kind of energy transfer that is central to thermodynamics. We return to these basic ideas several times throughout the next four chapters, and you will see that they affect everything from the behavior of atoms and molecules to cooking to our weather on Earth to the life cycles of stars.

Temperature and Thermal Equilibrium

By the end of this section, you will be able to:

- Define temperature and describe it qualitatively
- Explain thermal equilibrium
- Explain the zeroth law of thermodynamics

Heat is familiar to all of us. We can feel heat entering our bodies from the summer Sun or from hot coffee or tea after a winter stroll. We can also feel heat leaving our bodies as we feel the chill of night or the cooling effect of sweat after exercise.

What is heat? How do we define it and how is it related to temperature? What are the effects of heat and how does it flow from place to place? We will find that, in spite of the richness of the phenomena, a small set of underlying physical principles unites these subjects and ties them to other fields. We start by examining temperature and how to define and measure it.

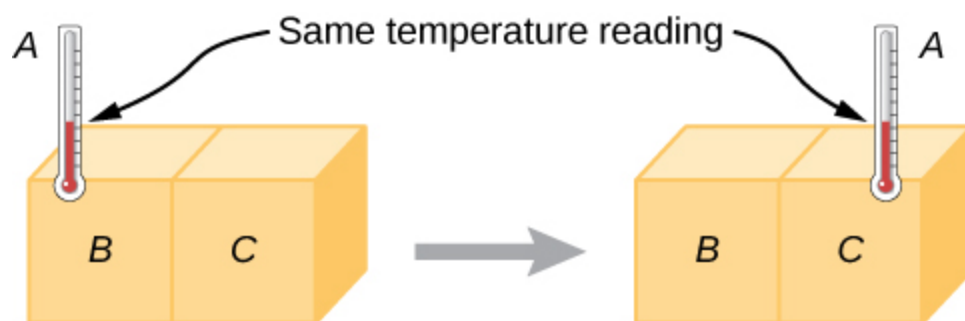
Temperature

The concept of temperature has evolved from the common concepts of hot and cold. The scientific definition of temperature explains more than our senses of hot and cold. As you may have already learned, many physical quantities are defined solely in terms of how they are observed or measured, that is, they are defined *operationally*. **Temperature** is operationally defined as the quantity of what we measure with a thermometer. As we will see in detail in a later chapter on the kinetic theory of gases, temperature is proportional to the average kinetic energy of translation, a fact that provides a more physical definition. Differences in temperature maintain the transfer of heat, or *heat transfer*, throughout the universe. **Heat transfer** is the movement of energy from one place or material to another as a result of a difference in temperature. (You will learn more about heat transfer later in this chapter.)

Thermal Equilibrium

An important concept related to temperature is **thermal equilibrium**. Two objects are in thermal equilibrium if they are in close contact that allows either to gain energy from the other, but nevertheless, no net energy is transferred between them. Even when not in contact, they are in thermal equilibrium if, when they are placed in contact, no net energy is transferred between them. If two objects remain in contact for a long time, they typically come to equilibrium. In other words, two objects in thermal equilibrium do not exchange energy.

Experimentally, if object *A* is in equilibrium with object *B*, and object *B* is in equilibrium with object *C*, then (as you may have already guessed) object *A* is in equilibrium with object *C*. That statement of transitivity is called the **zeroth law of thermodynamics**. (The number “zeroth” was suggested by British physicist Ralph Fowler in the 1930s. The first, second, and third laws of thermodynamics were already named and numbered then. The zeroth law had seldom been stated, but it needs to be discussed before the others, so Fowler gave it a smaller number.) Consider the case where *A* is a thermometer. The zeroth law tells us that if *A* reads a certain temperature when in equilibrium with *B*, and it is then placed in contact with *C*, it will not exchange energy with *C*; therefore, its temperature reading will remain the same ([\[link\]](#)). In other words, *if two objects are in thermal equilibrium, they have the same temperature*.



If thermometer *A* is in thermal equilibrium with object *B*, and *B* is in thermal equilibrium with *C*, then *A* is in thermal equilibrium with *C*. Therefore, the reading on *A* stays the same when *A* is moved over to make contact with *C*.

A thermometer measures its own temperature. It is through the concepts of thermal equilibrium and the zeroth law of thermodynamics that we can say that a thermometer measures the temperature of *something else*, and to make sense of the statement that two objects are at the same temperature.

In the rest of this chapter, we will often refer to “systems” instead of “objects.” As in the chapter on linear momentum and collisions, a system consists of one or more objects—but in thermodynamics, we require a system to be macroscopic, that is, to consist of a huge number (such as 10^{23}) of molecules. Then we can say that a system is in thermal equilibrium with itself if all parts of it are at the same temperature. (We will return to the definition of a thermodynamic system in the chapter on the first law of thermodynamics.)

Summary

- Temperature is operationally defined as the quantity measured by a thermometer. It is proportional to the average kinetic energy of atoms and molecules in a system.
- Thermal equilibrium occurs when two bodies are in contact with each other and can freely exchange energy. Systems are in thermal equilibrium when they have the same temperature.
- The zeroth law of thermodynamics states that when two systems, *A* and *B*, are in thermal equilibrium with each other, and *B* is in thermal equilibrium with a third system *C*, then *A* is also in thermal equilibrium with *C*.

Conceptual Questions

Exercise:

Problem:

What does it mean to say that two systems are in thermal equilibrium?

Solution:

They are at the same temperature, and if they are placed in contact, no net heat flows between them.

Exercise:**Problem:**

Give an example in which A has some kind of non-thermal equilibrium relationship with B , and B has the same relationship with C , but A does not have that relationship with C .

Glossary**heat transfer**

movement of energy from one place or material to another as a result of a difference in temperature

temperature

quantity measured by a thermometer, which reflects the mechanical energy of molecules in a system

thermal equilibrium

condition in which heat no longer flows between two objects that are in contact; the two objects have the same temperature

zeroth law of thermodynamics

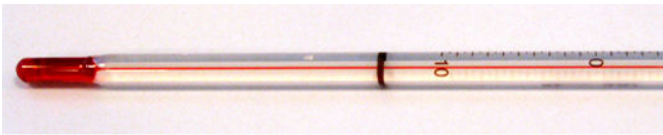
law that states that if two objects are in thermal equilibrium, and a third object is in thermal equilibrium with one of those objects, it is also in thermal equilibrium with the other object

Thermometers and Temperature Scales

By the end of this section, you will be able to:

- Describe several different types of thermometers
- Convert temperatures between the Celsius, Fahrenheit, and Kelvin scales

Any physical property that depends consistently and reproducibly on temperature can be used as the basis of a thermometer. For example, volume increases with temperature for most substances. This property is the basis for the common alcohol thermometer and the original mercury thermometers. Other properties used to measure temperature include electrical resistance, color, and the emission of infrared radiation ([\[link\]](#)).



(a)



(b)



(c)

Because many physical properties depend on temperature, the variety of thermometers is remarkable. (a) In this common type of thermometer, the alcohol, containing a red dye, expands more rapidly than the glass encasing it. When the thermometer's temperature increases, the liquid from the bulb is forced into the narrow tube, producing a large change in the length of the column for a small

change in temperature. (b) Each of the six squares on this plastic (liquid crystal) thermometer contains a film of a different heat-sensitive liquid crystal material. Below 95 °F, all six squares are black. When the plastic thermometer is exposed to a temperature of 95 °F, the first liquid crystal square changes color. When the temperature reaches above 96.8 °F, the second liquid crystal square also changes color, and so forth. (c) A firefighter uses a pyrometer to check the temperature of an aircraft carrier's ventilation system. The pyrometer measures infrared radiation (whose emission varies with temperature) from the vent and quickly produces a temperature readout. Infrared thermometers are also frequently used to measure body temperature by gently placing them in the ear canal. Such thermometers are more accurate than the alcohol thermometers placed under the tongue or in the armpit. (credit b: modification of work by Tess Watson; credit c: modification of work by Lamel J. Hinton, U.S. Navy)

Thermometers measure temperature according to well-defined scales of measurement. The three most common temperature scales are Fahrenheit, Celsius, and Kelvin. Temperature scales are created by identifying two reproducible temperatures. The freezing and boiling temperatures of water at standard atmospheric pressure are commonly used.

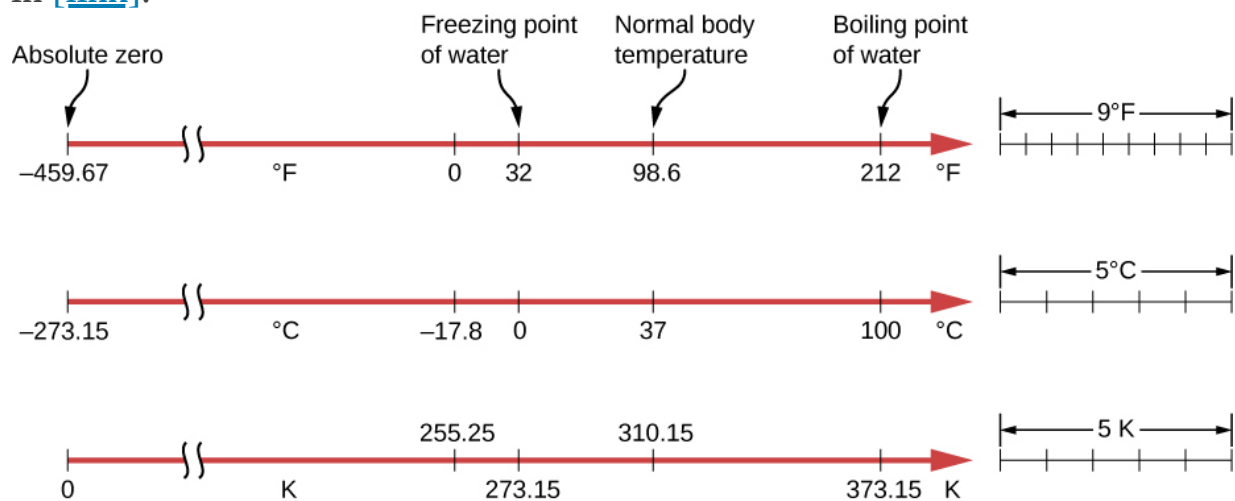
On the **Celsius scale**, the freezing point of water is 0 °C and the boiling point is 100 °C. The unit of temperature on this scale is the **degree Celsius** (°C). The **Fahrenheit scale** (still the most frequently used for common purposes in the United States) has the freezing point of water at 32 °F and the boiling point at 212 °F. Its unit is the **degree Fahrenheit** (°F). You can see that 100 Celsius degrees span the same range as 180 Fahrenheit degrees. Thus, a temperature difference of one degree on the Celsius scale is 1.8 times as large as a difference of one degree on the Fahrenheit scale, or $\Delta T_F = \frac{9}{5} \Delta T_C$.

The definition of temperature in terms of molecular motion suggests that there should be a lowest possible temperature, where the average kinetic

energy of molecules is zero (or the minimum allowed by quantum mechanics). Experiments confirm the existence of such a temperature, called **absolute zero**. An **absolute temperature scale** is one whose zero point is absolute zero. Such scales are convenient in science because several physical quantities, such as the volume of an ideal gas, are directly related to absolute temperature.

The **Kelvin scale** is the absolute temperature scale that is commonly used in science. The SI temperature unit is the *kelvin*, which is abbreviated K (not accompanied by a degree sign). Thus 0 K is absolute zero. The freezing and boiling points of water are 273.15 K and 373.15 K, respectively. Therefore, temperature differences are the same in units of kelvins and degrees Celsius, or $\Delta T_C = \Delta T_K$.

The relationships between the three common temperature scales are shown in [\[link\]](#). Temperatures on these scales can be converted using the equations in [\[link\]](#).



Relationships between the Fahrenheit, Celsius, and Kelvin temperature scales are shown. The relative sizes of the scales are also shown.

To convert from...	Use this equation...
Celsius to Fahrenheit	$T_F = \frac{9}{5}T_C + 32$
Fahrenheit to Celsius	$T_C = \frac{5}{9}(T_F - 32)$
Celsius to Kelvin	$T_K = T_C + 273.15$
Kelvin to Celsius	$T_C = T_K - 273.15$
Fahrenheit to Kelvin	$T_K = \frac{5}{9}(T_F - 32) + 273.15$
Kelvin to Fahrenheit	$T_F = \frac{9}{5}(T_K - 273.15) + 32$

Temperature Conversions

To convert between Fahrenheit and Kelvin, convert to Celsius as an intermediate step.

Example:

Converting between Temperature Scales: Room Temperature

“Room temperature” is generally defined in physics to be 25 °C. (a) What is room temperature in °F? (b) What is it in K?

Strategy

To answer these questions, all we need to do is choose the correct conversion equations and substitute the known values.

Solution

To convert from °C to °F, use the equation

Equation:

$$T_F = \frac{9}{5}T_C + 32.$$

Substitute the known value into the equation and solve:

Equation:

$$T_F = \frac{9}{5}(25\text{ }^\circ\text{C}) + 32 = 77\text{ }^\circ\text{F}.$$

Similarly, we find that $T_K = T_C + 273.15 = 298\text{ K}$.

The Kelvin scale is part of the SI system of units, so its actual definition is more complicated than the one given above. First, it is not defined in terms of the freezing and boiling points of water, but in terms of the **triple point**. The triple point is the unique combination of temperature and pressure at which ice, liquid water, and water vapor can coexist stably. As will be discussed in the section on phase changes, the coexistence is achieved by lowering the pressure and consequently the boiling point to reach the freezing point. The triple-point temperature is defined as 273.16 K. This definition has the advantage that although the freezing temperature and boiling temperature of water depend on pressure, there is only one triple-point temperature.

Second, even with two points on the scale defined, different thermometers give somewhat different results for other temperatures. Therefore, a standard thermometer is required. Metrologists (experts in the science of measurement) have chosen the *constant-volume gas thermometer* for this purpose. A vessel of constant volume filled with gas is subjected to temperature changes, and the measured temperature is proportional to the change in pressure. Using “TP” to represent the triple point,

Equation:

$$T = \frac{p}{p_{\text{TP}}} T_{\text{TP}}.$$

The results depend somewhat on the choice of gas, but the less dense the gas in the bulb, the better the results for different gases agree. If the results are extrapolated to zero density, the results agree quite well, with zero pressure corresponding to a temperature of absolute zero.

Constant-volume gas thermometers are big and come to equilibrium slowly, so they are used mostly as standards to calibrate other thermometers.

Note:

Visit this [site](#) to learn more about the constant-volume gas thermometer.

Summary

- Three types of thermometers are alcohol, liquid crystal, and infrared radiation (pyrometer).
- The three main temperature scales are Celsius, Fahrenheit, and Kelvin. Temperatures can be converted from one scale to another using temperature conversion equations.
- The three phases of water (ice, liquid water, and water vapor) can coexist at a single pressure and temperature known as the triple point.

Conceptual Questions

Exercise:

Problem:

If a thermometer is allowed to come to equilibrium with the air, and a glass of water is not in equilibrium with the air, what will happen to the thermometer reading when it is placed in the water?

Solution:

The reading will change.

Exercise:

Problem:

Give an example of a physical property that varies with temperature and describe how it is used to measure temperature.

Problems**Exercise:****Problem:**

While traveling outside the United States, you feel sick. A companion gets you a thermometer, which says your temperature is 39. What scale is that on? What is your Fahrenheit temperature? Should you seek medical help?

Solution:

That must be Celsius. Your Fahrenheit temperature is 102 °F. Yes, it is time to get treatment.

Exercise:

Problem: What are the following temperatures on the Kelvin scale?

- (a) 68.0 °F, an indoor temperature sometimes recommended for energy conservation in winter
- (b) 134 °F, one of the highest atmospheric temperatures ever recorded on Earth (Death Valley, California, 1913)
- (c) 9890 °F, the temperature of the surface of the Sun

Exercise:

Problem:

(a) Suppose a cold front blows into your locale and drops the temperature by 40.0 Fahrenheit degrees. How many degrees Celsius does the temperature decrease when it decreases by 40.0 °F? (b) Show that any change in temperature in Fahrenheit degrees is nine-fifths the change in Celsius degrees

Solution:

a. $\Delta T_C = 22.2^\circ \text{C}$; b. We know that $\Delta T_F = T_{F2} - T_{F1}$. We also know that $T_{F2} = \frac{9}{5}T_{C2} + 32$ and $T_{F1} = \frac{9}{5}T_{C1} + 32$. So, substituting, we have $\Delta T_F = \left(\frac{9}{5}T_{C2} + 32\right) - \left(\frac{9}{5}T_{C1} + 32\right)$. Partially solving and rearranging the equation, we have $\Delta T_F = \frac{9}{5}(T_{C2} - T_{C1})$. Therefore, $\Delta T_F = \frac{9}{5}\Delta T_C$.

Exercise:**Problem:**

An Associated Press article on climate change said, “Some of the ice shelf’s disappearance was probably during times when the planet was 36 degrees Fahrenheit (2 degrees Celsius) to 37 degrees Fahrenheit (3 degrees Celsius) warmer than it is today.” What mistake did the reporter make?

Exercise:**Problem:**

(a) At what temperature do the Fahrenheit and Celsius scales have the same numerical value? (b) At what temperature do the Fahrenheit and Kelvin scales have the same numerical value?

Solution:

a. -40° ; b. 575 K

Exercise:

Problem:

A person taking a reading of the temperature in a freezer in Celsius makes two mistakes: first omitting the negative sign and then thinking the temperature is Fahrenheit. That is, the person reads $-x\text{ }^{\circ}\text{C}$ as $x\text{ }^{\circ}\text{F}$. Oddly enough, the result is the correct Fahrenheit temperature. What is the original Celsius reading? Round your answer to three significant figures.

Glossary

absolute temperature scale

scale, such as Kelvin, with a zero point that is absolute zero

absolute zero

temperature at which the average kinetic energy of molecules is zero

Celsius scale

temperature scale in which the freezing point of water is $0\text{ }^{\circ}\text{C}$ and the boiling point of water is $100\text{ }^{\circ}\text{C}$

degree Celsius

($^{\circ}\text{C}$) unit on the Celsius temperature scale

degree Fahrenheit

($^{\circ}\text{F}$) unit on the Fahrenheit temperature scale

Fahrenheit scale

temperature scale in which the freezing point of water is $32\text{ }^{\circ}\text{F}$ and the boiling point of water is $212\text{ }^{\circ}\text{F}$

Kelvin scale (K)

temperature scale in which 0 K is the lowest possible temperature, representing absolute zero

triple point

pressure and temperature at which a substance exists in equilibrium as a solid, liquid, and gas

Thermal Expansion

By the end of this section, you will be able to:

- Answer qualitative questions about the effects of thermal expansion
- Solve problems involving thermal expansion, including those involving thermal stress

The expansion of alcohol in a thermometer is one of many commonly encountered examples of **thermal expansion**, which is the change in size or volume of a given system as its temperature changes. The most visible example is the expansion of hot air. When air is heated, it expands and becomes less dense than the surrounding air, which then exerts an (upward) force on the hot air and makes steam and smoke rise, hot air balloons float, and so forth. The same behavior happens in all liquids and gases, driving natural heat transfer upward in homes, oceans, and weather systems, as we will discuss in an upcoming section. Solids also undergo thermal expansion. Railroad tracks and bridges, for example, have expansion joints to allow them to freely expand and contract with temperature changes, as shown in [\[link\]](#).



(a)



(b)

(a) Thermal expansion joints like these in the (b) Auckland Harbour Bridge in New Zealand allow bridges to change length without buckling. (credit: modification of works by “ŠJů”/Wikimedia Commons)

What is the underlying cause of thermal expansion? As previously mentioned, an increase in temperature means an increase in the kinetic energy of individual atoms. In a solid, unlike in a gas, the molecules are held in place by forces from neighboring molecules; as we saw in [Oscillations](#), the forces can be modeled as in harmonic springs described by the Lennard-Jones potential. [Energy in Simple Harmonic Motion](#) shows that such potentials are asymmetrical in that the potential energy increases more steeply when the molecules get closer to each other than when they get farther away. Thus, at a given kinetic energy, the distance moved is greater when neighbors move away from each other than when they move toward each other. The result is that increased kinetic energy (increased temperature) increases the average distance between molecules—the substance expands.

For most substances under ordinary conditions, it is an excellent approximation that there is no preferred direction (that is, the solid is “isotropic”), and an increase in temperature increases the solid’s size by a

certain fraction in each dimension. Therefore, if the solid is free to expand or contract, its proportions stay the same; only its overall size changes.

Note:
Linear Thermal Expansion
According to experiments, the dependence of thermal expansion on temperature, substance, and original length is summarized in the equation
Equation:
$$\frac{dL}{dT} = \alpha L$$

where ΔL is the change in length L , ΔT is the change in temperature, and α is the **coefficient of linear expansion**, a material property that varies slightly with temperature. As α is nearly constant and also very small, for practical purposes, we use the linear approximation:
Equation:
$$\Delta L = \alpha L \Delta T.$$

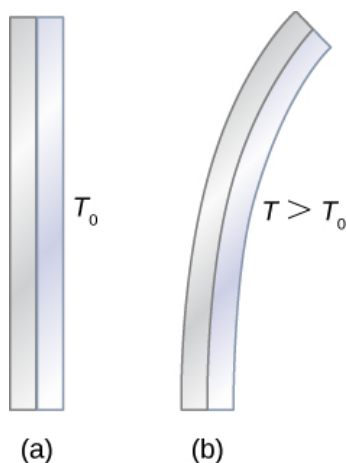
[\[link\]](#) lists representative values of the coefficient of linear expansion. As noted earlier, ΔT is the same whether it is expressed in units of degrees Celsius or kelvins; thus, α may have units of $1/^{\circ}\text{C}$ or $1/\text{K}$ with the same value in either case. Approximating α as a constant is quite accurate for small changes in temperature and sufficient for most practical purposes, even for large changes in temperature. We examine this approximation more closely in the next example.

Material	Coefficient of Linear Expansion α ($1/^{\circ}\text{C}$)	Coefficient of Volume Expansion β ($1/^{\circ}\text{C}$)
<i>Solids</i>		
Aluminum	25×10^{-6}	75×10^{-6}
Brass	19×10^{-6}	56×10^{-6}
Copper	17×10^{-6}	51×10^{-6}
Gold	14×10^{-6}	42×10^{-6}
Iron or steel	12×10^{-6}	35×10^{-6}
Invar (nickel-iron alloy)	0.9×10^{-6}	2.7×10^{-6}

Material	Coefficient of Linear Expansion α ($1/^{\circ}\text{C}$)	Coefficient of Volume Expansion β ($1/^{\circ}\text{C}$)
Lead	29×10^{-6}	87×10^{-6}
Silver	18×10^{-6}	54×10^{-6}
Glass (ordinary)	9×10^{-6}	27×10^{-6}
Glass (Pyrex®)	3×10^{-6}	9×10^{-6}
Quartz	0.4×10^{-6}	1×10^{-6}
Concrete, brick	$\sim 12 \times 10^{-6}$	$\sim 36 \times 10^{-6}$
Marble (average)	2.5×10^{-6}	7.5×10^{-6}
<i>Liquids</i>		
Ether		1650×10^{-6}
Ethyl alcohol		1100×10^{-6}
Gasoline		950×10^{-6}
Glycerin		500×10^{-6}
Mercury		180×10^{-6}
Water		210×10^{-6}
<i>Gases</i>		
Air and most other gases at atmospheric pressure		3400×10^{-6}

Thermal Expansion Coefficients

Thermal expansion is exploited in the bimetallic strip ([link](#)). This device can be used as a thermometer if the curving strip is attached to a pointer on a scale. It can also be used to automatically close or open a switch at a certain temperature, as in older or analog thermostats.



The curvature of a bimetallic strip depends on temperature. (a) The strip is straight at the starting temperature, where its two components have the same length. (b) At a higher temperature, this strip bends to the right, because the metal on the left has expanded more than the metal on the right. At a lower temperature, the strip would bend to the left.

Example:

Calculating Linear Thermal Expansion

The main span of San Francisco's Golden Gate Bridge is 1275 m long at its coldest. The bridge is exposed to temperatures ranging from -15°C to 40°C . What is its change in length between these temperatures? Assume that the bridge is made entirely of steel.

Strategy

Use the equation for linear thermal expansion $\Delta L = \alpha L \Delta T$ to calculate the change in length, ΔL . Use the coefficient of linear expansion α for steel from [\[link\]](#), and note that the change in temperature ΔT is 55°C .

Solution

Substitute all of the known values into the equation to solve for ΔL :

Equation:

$$\Delta L = \alpha L \Delta T = \left(\frac{12 \times 10^{-6}}{^\circ\text{C}} \right) (1275 \text{ m}) (55^\circ\text{C}) = 0.84 \text{ m}.$$

Significance

Although not large compared with the length of the bridge, this change in length is observable. It is generally spread over many expansion joints so that the expansion at each joint is small.

Thermal Expansion in Two and Three Dimensions

Unconstrained objects expand in all dimensions, as illustrated in [\[link\]](#). That is, their areas and volumes, as well as their lengths, increase with temperature. Because the proportions stay the same, holes and container volumes also get larger with temperature. If you cut a hole in a metal plate, the remaining material will expand exactly as it would if the piece you removed were still in place. The piece would get bigger, so the hole must get bigger too.

Note:

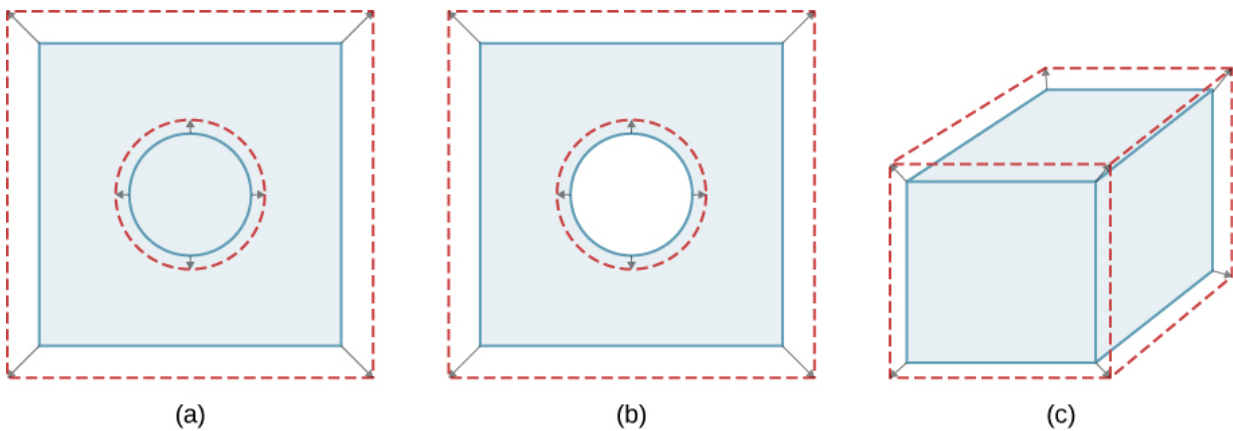
Thermal Expansion in Two Dimensions

For small temperature changes, the change in area ΔA is given by

Equation:

$$\Delta A = 2\alpha A \Delta T$$

where ΔA is the change in area A , ΔT is the change in temperature, and α is the coefficient of linear expansion, which varies slightly with temperature. (The derivation of this equation is analogous to that of the more important equation for three dimensions, below.)



In general, objects expand in all directions as temperature increases. In these drawings, the original boundaries of the objects are shown with solid lines, and the expanded boundaries with dashed lines.

(a) Area increases because both length and width increase. The area of a circular plug also increases.

(b) If the plug is removed, the hole it leaves becomes larger with increasing temperature, just as if the expanding plug were still in place. (c) Volume also increases, because all three dimensions increase.

Note:**Thermal Expansion in Three Dimensions**

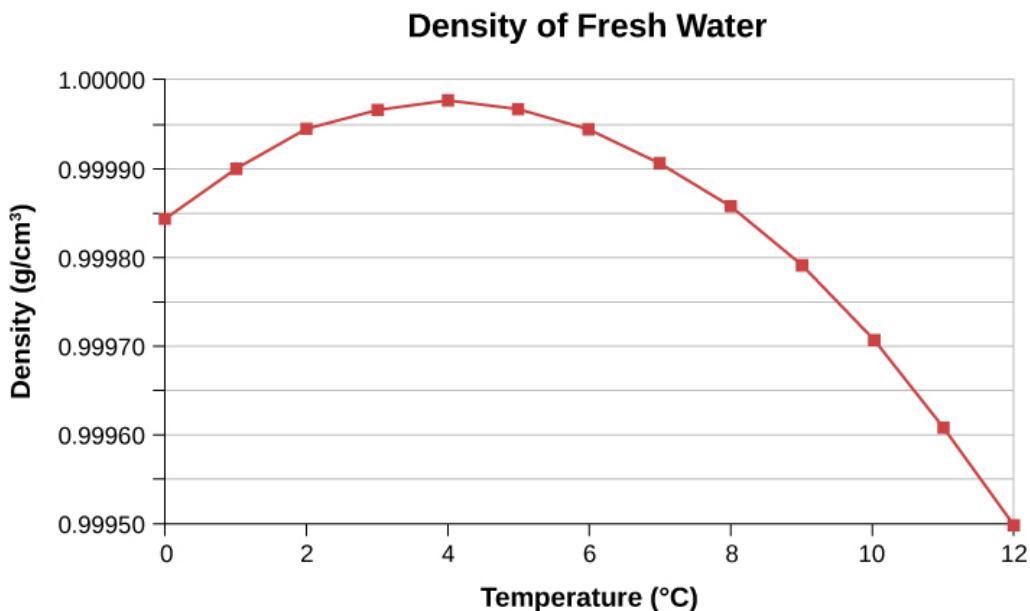
The relationship between volume and temperature $\frac{dV}{dT}$ is given by $\frac{dV}{dT} = \beta V \Delta T$, where β is the **coefficient of volume expansion**. As you can show in [\[link\]](#), $\beta = 3\alpha$. This equation is usually written as **Equation:**

$$\Delta V = \beta V \Delta T.$$

Note that the values of β in [\[link\]](#) are equal to 3α except for rounding.

Volume expansion is defined for liquids, but linear and area expansion are not, as a liquid's changes in linear dimensions and area depend on the shape of its container. Thus, [\[link\]](#) shows liquids' values of β but not α .

In general, objects expand with increasing temperature. Water is the most important exception to this rule. Water does expand with increasing temperature (its density *decreases*) at temperatures greater than 4 °C (40 °F). However, it is densest at +4 °C and expands with *decreasing* temperature between +4 °C and 0 °C (40 °F to 32 °F), as shown in [\[link\]](#). A striking effect of this phenomenon is the freezing of water in a pond. When water near the surface cools down to 4 °C, it is denser than the remaining water and thus sinks to the bottom. This “turnover” leaves a layer of warmer water near the surface, which is then cooled. However, if the temperature in the surface layer drops below 4 °C, that water is less dense than the water below, and thus stays near the top. As a result, the pond surface can freeze over. The layer of ice insulates the liquid water below it from low air temperatures. Fish and other aquatic life can survive in 4 °C water beneath ice, due to this unusual characteristic of water.



This curve shows the density of water as a function of temperature. Note that the thermal expansion at low temperatures is very small. The maximum density at 4 °C is only 0.0075 % greater than the density at 2 °C, and 0.012 % greater than that at 0 °C. The decrease of density below 4 °C occurs because the liquid water

approaches the solid crystal form of ice, which contains more empty space than the liquid.

Example:**Calculating Thermal Expansion**

Suppose your 60.0-L (15.9 -gal-gal) steel gasoline tank is full of gas that is cool because it has just been pumped from an underground reservoir. Now, both the tank and the gasoline have a temperature of 15.0 °C. How much gasoline has spilled by the time they warm to 35.0 °C?

Strategy

The tank and gasoline increase in volume, but the gasoline increases more, so the amount spilled is the difference in their volume changes. We can use the equation for volume expansion to calculate the change in volume of the gasoline and of the tank. (The gasoline tank can be treated as solid steel.)

Solution

1. Use the equation for volume expansion to calculate the increase in volume of the steel tank:

Equation:

$$\Delta V_s = \beta_s V_s \Delta T.$$

2. The increase in volume of the gasoline is given by this equation:

Equation:

$$\Delta V_{\text{gas}} = \beta_{\text{gas}} V_{\text{gas}} \Delta T.$$

3. Find the difference in volume to determine the amount spilled as

Equation:

$$V_{\text{spill}} = \Delta V_{\text{gas}} - \Delta V_s.$$

Alternatively, we can combine these three equations into a single equation. (Note that the original volumes are equal.)

Equation:

$$\begin{aligned} V_{\text{spill}} &= (\beta_{\text{gas}} - \beta_s) V \Delta T \\ &= [(950 - 35) \times 10^{-6} / ^\circ\text{C}] (60.0 \text{ L}) (20.0 ^\circ\text{C}) \\ &= 1.10 \text{ L.} \end{aligned}$$

Significance

This amount is significant, particularly for a 60.0-L tank. The effect is so striking because the gasoline and steel expand quickly. The rate of change in thermal properties is discussed later in this chapter. If you try to cap the tank tightly to prevent overflow, you will find that it leaks anyway, either around the cap or by bursting the tank. Tightly constricting the expanding gas is equivalent to compressing it, and both liquids and solids resist compression with extremely large forces. To avoid rupturing rigid containers, these containers have air gaps, which allow them to expand and contract without stressing them.

Note:**Exercise:****Problem:**

Check Your Understanding Does a given reading on a gasoline gauge indicate more gasoline in cold weather or in hot weather, or does the temperature not matter?

Solution:

The actual amount (mass) of gasoline left in the tank when the gauge hits “empty” is less in the summer than in the winter. The gasoline has the same volume as it does in the winter when the “add fuel” light goes on, but because the gasoline has expanded, there is less mass.

Thermal Stress

If you change the temperature of an object while preventing it from expanding or contracting, the object is subjected to stress that is compressive if the object would expand in the absence of constraint and tensile if it would contract. This stress resulting from temperature changes is known as **thermal stress**. It can be quite large and can cause damage.

To avoid this stress, engineers may design components so they can expand and contract freely. For instance, in highways, gaps are deliberately left between blocks to prevent thermal stress from developing. When no gaps can be left, engineers must consider thermal stress in their designs. Thus, the reinforcing rods in concrete are made of steel because steel’s coefficient of linear expansion is nearly equal to that of concrete.

To calculate the thermal stress in a rod whose ends are both fixed rigidly, we can think of the stress as developing in two steps. First, let the ends be free to expand (or contract) and find the expansion (or contraction). Second, find the stress necessary to compress (or extend) the rod to its original length by the methods you studied in [Static Equilibrium and Elasticity](#) on static equilibrium and elasticity. In other words, the ΔL of the thermal expansion equals the ΔL of the elastic distortion (except that the signs are opposite).

Example:**Calculating Thermal Stress**

Concrete blocks are laid out next to each other on a highway without any space between them, so they cannot expand. The construction crew did the work on a winter day when the temperature was 5°C . Find the stress in the blocks on a hot summer day when the temperature is 38°C . The compressive Young’s modulus of concrete is $Y = 20 \times 10^9 \text{ N/m}^2$.

Strategy

According to the chapter on static equilibrium and elasticity, the stress F/A is given by

Equation:

$$\frac{F}{A} = Y \frac{\Delta L}{L_0},$$

where Y is the Young’s modulus of the material—concrete, in this case. In thermal expansion, $\Delta L = \alpha L_0 \Delta T$. We combine these two equations by noting that the two ΔL /s are equal, as stated above.

Because we are not given L_0 or A , we can obtain a numerical answer only if they both cancel out.

Solution

We substitute the thermal-expansion equation into the elasticity equation to get

Equation:

$$\frac{F}{A} = Y \frac{\alpha L_0 \Delta T}{L_0} = Y \alpha \Delta T,$$

and as we hoped, L_0 has canceled and A appears only in F/A , the notation for the quantity we are calculating.

Now we need only insert the numbers:

Equation:

$$\frac{F}{A} = (20 \times 10^9 \text{ N/m}^2) (12 \times 10^{-6} / ^\circ\text{C}) (38 ^\circ\text{C} - 5 ^\circ\text{C}) = 7.9 \times 10^6 \text{ N/m}^2.$$

Significance

The ultimate compressive strength of concrete is $20 \times 10^6 \text{ N/m}^2$, so the blocks are unlikely to break. However, the ultimate shear strength of concrete is only $2 \times 10^6 \text{ N/m}^2$, so some might chip off.

Note:

Exercise:

Problem:

Check Your Understanding Two objects A and B have the same dimensions and are constrained identically. A is made of a material with a higher thermal expansion coefficient than B . If the objects are heated identically, will A feel a greater stress than B ?

Solution:

Not necessarily, as the thermal stress is also proportional to Young's modulus.

Summary

- Thermal expansion is the increase of the size (length, area, or volume) of a body due to a change in temperature, usually a rise. Thermal contraction is the decrease in size due to a change in temperature, usually a fall in temperature.
- Thermal stress is created when thermal expansion or contraction is constrained.

Conceptual Questions

Exercise:

Problem:

Pouring cold water into hot glass or ceramic cookware can easily break it. What causes the breaking? Explain why Pyrex®, a glass with a small coefficient of linear expansion, is less susceptible.

Solution:

The cold water cools part of the inner surface, making it contract, while the rest remains expanded. The strain is too great for the strength of the material. Pyrex contracts less, so it experiences less strain.

Exercise:**Problem:**

One method of getting a tight fit, say of a metal peg in a hole in a metal block, is to manufacture the peg slightly larger than the hole. The peg is then inserted when at a different temperature than the block. Should the block be hotter or colder than the peg during insertion? Explain your answer.

Exercise:**Problem:**

Does it really help to run hot water over a tight metal lid on a glass jar before trying to open it? Explain your answer.

Solution:

In principle, the lid expands more than the jar because metals have higher coefficients of expansion than glass. That should make unscrewing the lid easier. (In practice, getting the lid and jar wet may make gripping them more difficult.)

Exercise:**Problem:**

When a cold alcohol thermometer is placed in a hot liquid, the column of alcohol goes *down* slightly before going up. Explain why.

Exercise:**Problem:**

Calculate the length of a 1-meter rod of a material with thermal expansion coefficient α when the temperature is raised from 300 K to 600 K. Taking your answer as the new initial length, find the length after the rod is cooled back down to 300 K. Is your answer 1 meter? Should it be? How can you account for the result you got?

Solution:

After being heated, the length is $(1 + 300\alpha)$ (1 m). After being cooled, the length is $(1 - 300\alpha)(1 + 300\alpha)$ (1 m). That answer is not 1 m, but it should be. The explanation is that even if α is exactly constant, the relation $\Delta L = \alpha L \Delta T$ is strictly true only in the limit of small ΔT . Since α values are small, the discrepancy is unimportant in practice.

Exercise:

Problem:

Noting the large stresses that can be caused by thermal expansion, an amateur weapon inventor decides to use it to make a new kind of gun. He plans to jam a bullet against an aluminum rod inside a closed invar tube. When he heats the tube, the rod will expand more than the tube and a very strong force will build up. Then, by a method yet to be determined, he will open the tube in a split second and let the force of the rod launch the bullet at very high speed. What is he overlooking?

Problems**Exercise:****Problem:**

The height of the Washington Monument is measured to be 170.00 m on a day when the temperature is $35.0\text{ }^{\circ}\text{C}$. What will its height be on a day when the temperature falls to $-10.0\text{ }^{\circ}\text{C}$? Although the monument is made of limestone, assume that its coefficient of thermal expansion is the same as that of marble. Give your answer to five significant figures.

Solution:

Using [\[link\]](#) to find the coefficient of thermal expansion of marble:

$$L = L_0 + \Delta L = L_0 (1 + \alpha \Delta T) = 170\text{ m} [1 + (2.5 \times 10^{-6}/^{\circ}\text{C}) (-45.0\text{ }^{\circ}\text{C})] = 169.98\text{ m.}$$

(Answer rounded to five significant figures to show the slight difference in height.)

Exercise:**Problem:**

How much taller does the Eiffel Tower become at the end of a day when the temperature has increased by $15\text{ }^{\circ}\text{C}$? Its original height is 321 m and you can assume it is made of steel.

Exercise:**Problem:**

What is the change in length of a 3.00-cm-long column of mercury if its temperature changes from $37.0\text{ }^{\circ}\text{C}$ to $40.0\text{ }^{\circ}\text{C}$, assuming the mercury is constrained to a cylinder but unconstrained in length? Your answer will show why thermometers contain bulbs at the bottom instead of simple columns of liquid.

Solution:

Using [\[link\]](#) to find the coefficient of thermal expansion of mercury:

$$\Delta L = \alpha L \Delta T = (6.0 \times 10^{-5}/^{\circ}\text{C}) (0.0300\text{ m}) (3.00\text{ }^{\circ}\text{C}) = 5.4 \times 10^{-6}\text{ m.}$$

Exercise:**Problem:**

How large an expansion gap should be left between steel railroad rails if they may reach a maximum temperature $35.0\text{ }^{\circ}\text{C}$ greater than when they were laid? Their original length is 10.0 m.

Exercise:

Problem:

You are looking to buy a small piece of land in Hong Kong. The price is “only” \$60,000 per square meter. The land title says the dimensions are 20 m \times 30 m. By how much would the total price change if you measured the parcel with a steel tape measure on a day when the temperature was 20 °C above the temperature that the tape measure was designed for? The dimensions of the land do not change.

Solution:

On the warmer day, our tape measure will expand linearly. Therefore, each measured dimension will be smaller than the actual dimension of the land. Calling these measured dimensions l' and w' , we will find a new area, A . Let's calculate these measured dimensions:

$$l' = l_0 - \Delta l = (20 \text{ m}) - (20^\circ\text{C})(20 \text{ m}) \left(\frac{1.2 \times 10^{-5}}{^\circ\text{C}} \right) = 19.9952 \text{ m};$$

$$A' = l' \times w' = (19.9952 \text{ m})(19.9952 \text{ m}) = 399.808 \text{ m}^2;$$

$$\text{Cost change} = (A - A') \left(\frac{\$60,000}{\text{m}^2} \right) = ((600 - 399.808) \text{ m}^2) \left(\frac{\$60,000}{\text{m}^2} \right) = \$12,012.$$

Because the area gets smaller, the price of the land *decreases* by about \$12,012.

Exercise:**Problem:**

Global warming will produce rising sea levels partly due to melting ice caps and partly due to the expansion of water as average ocean temperatures rise. To get some idea of the size of this effect, calculate the change in length of a column of water 1.00 km high for a temperature increase of 1.00 °C. Assume the column is not free to expand sideways. As a model of the ocean, that is a reasonable approximation, as only parts of the ocean very close to the surface can expand sideways onto land, and only to a limited degree. As another approximation, neglect the fact that ocean warming is not uniform with depth.

Exercise:**Problem:**

(a) Suppose a meter stick made of steel and one made of aluminum are the same length at 0 °C. What is their difference in length at 22.0 °C? (b) Repeat the calculation for two 30.0-m-long surveyor's tapes.

Solution:

a. Use [\[link\]](#) to find the coefficients of thermal expansion of steel and aluminum. Then

$$\Delta L_{\text{Al}} - \Delta L_{\text{steel}} = (\alpha_{\text{Al}} - \alpha_{\text{steel}})L_0\Delta T = \left(\frac{2.5 \times 10^{-5}}{^\circ\text{C}} - \frac{1.2 \times 10^{-5}}{^\circ\text{C}} \right)(1.00 \text{ m})(22^\circ\text{C}) = 2.9 \times 10^{-4} \text{ m}$$

b. By the same method with $L_0 = 30.0 \text{ m}$, we have $\Delta L = 8.6 \times 10^{-3} \text{ m}$.

Exercise:**Problem:**

(a) If a 500-mL glass beaker is filled to the brim with ethyl alcohol at a temperature of 5.00 °C, how much will overflow when the alcohol's temperature reaches the room temperature of 22.0 °C? (b) How much less water would overflow under the same conditions?

Exercise:

Problem:

Most cars have a coolant reservoir to catch radiator fluid that may overflow when the engine is hot. A radiator is made of copper and is filled to its 16.0-L capacity when at 10.0 °C. What volume of radiator fluid will overflow when the radiator and fluid reach a temperature of 95.0 °C, given that the fluid's volume coefficient of expansion is $\beta = 400 \times 10^{-6}/^{\circ}\text{C}$? (Your answer will be a conservative estimate, as most car radiators have operating temperatures greater than 95.0 °C).

Solution:

$$\Delta V = 0.475 \text{ L}$$

Exercise:**Problem:**

A physicist makes a cup of instant coffee and notices that, as the coffee cools, its level drops 3.00 mm in the glass cup. Show that this decrease cannot be due to thermal contraction by calculating the decrease in level if the 350 cm³ of coffee is in a 7.00-cm-diameter cup and decreases in temperature from 95.0 °C to 45.0 °C. (Most of the drop in level is actually due to escaping bubbles of air.)

Exercise:**Problem:**

The density of water at 0 °C is very nearly 1000 kg/m³ (it is actually 999.84 kg/m³), whereas the density of ice at 0 °C is 917 kg/m³. Calculate the pressure necessary to keep ice from expanding when it freezes, neglecting the effect such a large pressure would have on the freezing temperature. (This problem gives you only an indication of how large the forces associated with freezing water might be.)

Solution:

If we start with the freezing of water, then it would expand to

$$(1 \text{ m}^3) \left(\frac{1000 \text{ kg/m}^3}{917 \text{ kg/m}^3} \right) = 1.09 \text{ m}^3 = 1.98 \times 10^8 \text{ N/m}^2 \text{ of ice.}$$
Exercise:**Problem:**

Show that $\beta = 3\alpha$, by calculating the infinitesimal change in volume dV of a cube with sides of length L when the temperature changes by dT .

Glossary

coefficient of linear expansion

(α) material property that gives the change in length, per unit length, per 1-°C change in temperature; a constant used in the calculation of linear expansion; the coefficient of linear expansion depends to some degree on the temperature of the material

coefficient of volume expansion

(β) similar to α but gives the change in volume, per unit volume, per 1-°C change in temperature

thermal expansion

change in size or volume of an object with change in temperature

thermal stress

stress caused by thermal expansion or contraction

Heat Transfer, Specific Heat, and Calorimetry

By the end of this section, you will be able to:

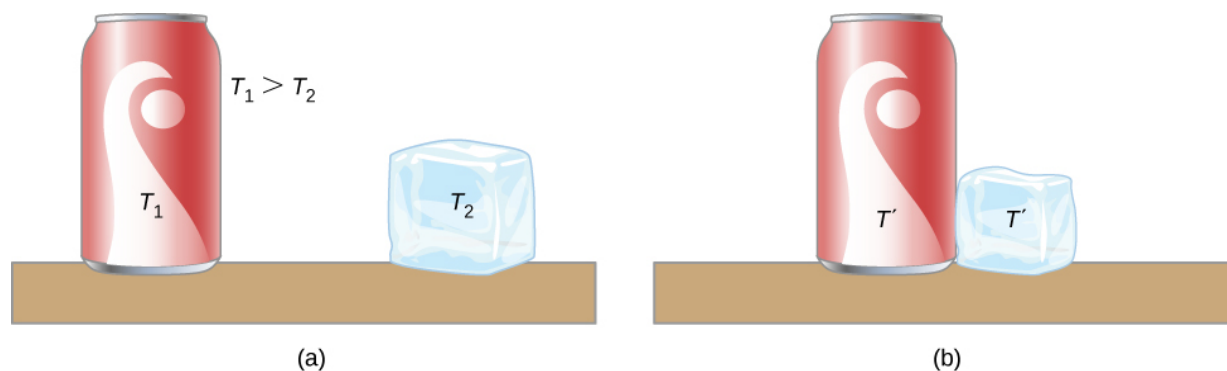
- Explain phenomena involving heat as a form of energy transfer
- Solve problems involving heat transfer

We have seen in previous chapters that energy is one of the fundamental concepts of physics. **Heat** is a type of energy transfer that is caused by a temperature difference, and it can change the temperature of an object. As we learned earlier in this chapter, heat transfer is the movement of energy from one place or material to another as a result of a difference in temperature. Heat transfer is fundamental to such everyday activities as home heating and cooking, as well as many industrial processes. It also forms a basis for the topics in the remainder of this chapter.

We also introduce the concept of internal energy, which can be increased or decreased by heat transfer. We discuss another way to change the internal energy of a system, namely doing work on it. Thus, we are beginning the study of the relationship of heat and work, which is the basis of engines and refrigerators and the central topic (and origin of the name) of thermodynamics.

Internal Energy and Heat

A thermal system has *internal energy* (also called thermal energy), which is the sum of the mechanical energies of its molecules. A system's internal energy is proportional to its temperature. As we saw earlier in this chapter, if two objects at different temperatures are brought into contact with each other, energy is transferred from the hotter to the colder object until the bodies reach thermal equilibrium (that is, they are at the same temperature). No work is done by either object because no force acts through a distance (as we discussed in [Work and Kinetic Energy](#)). These observations reveal that heat is energy transferred spontaneously due to a temperature difference. [\[link\]](#) shows an example of heat transfer.



(a) Here, the soft drink has a higher temperature than the ice, so they are not in thermal equilibrium. (b) When the soft drink and ice are allowed to interact, heat is transferred from the drink to the ice due to the difference in temperatures until they reach the same temperature, T' , achieving equilibrium. In fact, since the soft drink and ice are both in contact with the surrounding air and the bench, the ultimate equilibrium temperature will be the same as that of the surroundings.

The meaning of “heat” in physics is different from its ordinary meaning. For example, in conversation, we may say “the heat was unbearable,” but in physics, we would say that the temperature was high. Heat is a form of energy flow, whereas temperature is not. Incidentally, humans are sensitive to *heat flow* rather than to temperature.

Since heat is a form of energy, its SI unit is the joule (J). Another common unit of energy often used for heat is the **calorie** (cal), defined as the energy needed to change the temperature of 1.00 g of water by 1.00 °C—specifically, between 14.5 °C and 15.5 °C, since there is a slight temperature dependence. Also commonly used is the **kilocalorie** (kcal), which is the energy needed to change the temperature of 1.00 kg of water by 1.00 °C. Since mass is most often specified in kilograms, the kilocalorie is convenient. Confusingly, food calories (sometimes called “big calories,” abbreviated Cal) are actually kilocalories, a fact not easily determined from package labeling.

Mechanical Equivalent of Heat

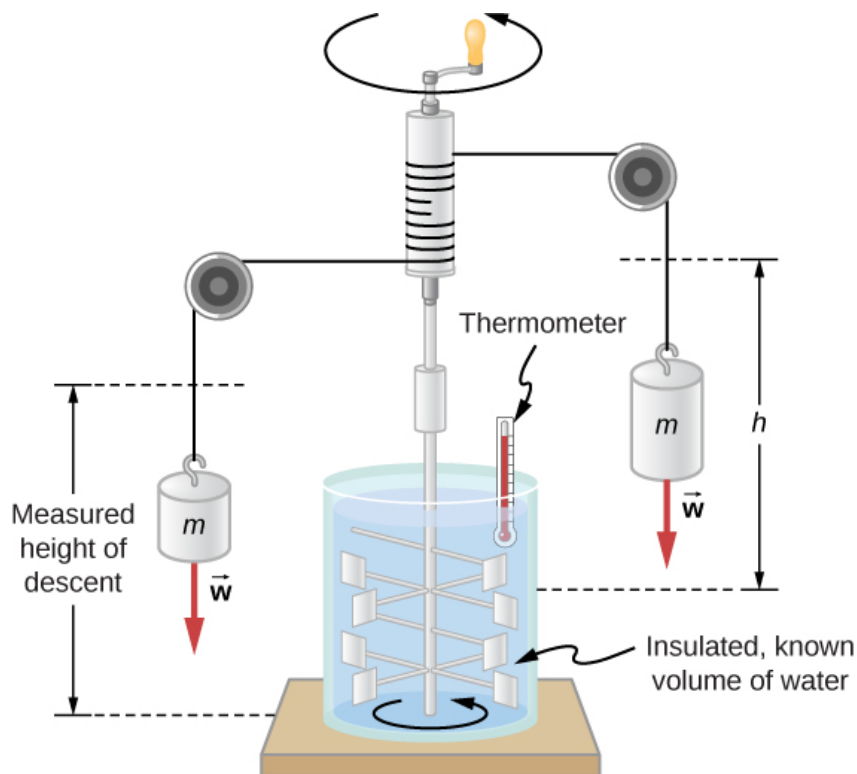
It is also possible to change the temperature of a substance by doing work, which transfers energy into or out of a system. This realization helped establish that heat is a form of energy. James Prescott Joule (1818–1889) performed many experiments to establish the **mechanical equivalent of heat**—*the work needed to produce the same effects as heat transfer*. In the units used for these two quantities, the value for this equivalence is

Equation:

$$1.000 \text{ kcal} = 4186 \text{ J.}$$

We consider this equation to represent the conversion between two units of energy. (Other numbers that you may see refer to calories defined for temperature ranges other than 14.5 °C to 15.5 °C.)

[\[link\]](#) shows one of Joule’s most famous experimental setups for demonstrating that work and heat can produce the same effects and measuring the mechanical equivalent of heat. It helped establish the principle of conservation of energy. Gravitational potential energy (U) was converted into kinetic energy (K), and then randomized by viscosity and turbulence into increased average kinetic energy of atoms and molecules in the system, producing a temperature increase. Joule’s contributions to thermodynamics were so significant that the SI unit of energy was named after him.



Joule's experiment established the equivalence of heat and work.

As the masses descended, they caused the paddles to do work, $W = mgh$, on the water. The result was a temperature increase, ΔT , measured by the thermometer. Joule found that ΔT was proportional to W and thus determined the mechanical equivalent of heat.

Increasing internal energy by heat transfer gives the same result as increasing it by doing work. Therefore, although a system has a well-defined internal energy, we cannot say that it has a certain "heat content" or "work content." A well-defined quantity that depends only on the current state of the system, rather than on the history of that system, is known as a *state variable*. Temperature and internal energy are state variables. To sum up this paragraph, *heat and work are not state variables*.

Incidentally, increasing the internal energy of a system does not necessarily increase its temperature. As we'll see in the next section, the temperature does not change when a substance changes from one phase to another. An example is the melting of ice, which can be accomplished by adding heat or by doing frictional work, as when an ice cube is rubbed against a rough surface.

Temperature Change and Heat Capacity

We have noted that heat transfer often causes temperature change. Experiments show that with no phase change and no work done on or by the system, the transferred heat is typically directly proportional to the change in temperature and to the mass of the system, to a good approximation. (Below we show how to handle situations where the approximation is not valid.) The constant of

proportionality depends on the substance and its phase, which may be gas, liquid, or solid. We omit discussion of the fourth phase, plasma, because although it is the most common phase in the universe, it is rare and short-lived on Earth.

We can understand the experimental facts by noting that the transferred heat is the change in the internal energy, which is the total energy of the molecules. Under typical conditions, the total kinetic energy of the molecules K_{total} is a constant fraction of the internal energy (for reasons and with exceptions that we'll see in the next chapter). The average kinetic energy of a molecule K_{ave} is proportional to the absolute temperature. Therefore, the change in internal energy of a system is typically proportional to the change in temperature and to the number of molecules, N . Mathematically, $\Delta U \propto \Delta K_{\text{total}} = NK_{\text{ave}} \propto N\Delta T$. The dependence on the substance results in large part from the different masses of atoms and molecules. We are considering its heat capacity in terms of its mass, but as we will see in the next chapter, in some cases, heat capacities *per molecule* are similar for different substances. The dependence on substance and phase also results from differences in the potential energy associated with interactions between atoms and molecules.

Note:

Heat Transfer and Temperature Change

A practical approximation for the relationship between heat transfer and temperature change is:

Equation:

$$Q = mc\Delta T,$$

where Q is the symbol for heat transfer (“quantity of heat”), m is the mass of the substance, and ΔT is the change in temperature. The symbol c stands for the **specific heat** (also called “*specific heat capacity*”) and depends on the material and phase. The specific heat is numerically equal to the amount of heat necessary to change the temperature of 1.00 kg of mass by 1.00 °C. The SI unit for specific heat is J/(kg × K) or J/(kg × °C). (Recall that the temperature change ΔT is the same in units of kelvin and degrees Celsius.)

Values of specific heat must generally be measured, because there is no simple way to calculate them precisely. [\[link\]](#) lists representative values of specific heat for various substances. We see from this table that the specific heat of water is five times that of glass and 10 times that of iron, which means that it takes five times as much heat to raise the temperature of water a given amount as for glass, and 10 times as much as for iron. In fact, water has one of the largest specific heats of any material, which is important for sustaining life on Earth.

The specific heats of gases depend on what is maintained constant during the heating—typically either the volume or the pressure. In the table, the first specific heat value for each gas is measured at constant volume, and the second (in parentheses) is measured at constant pressure. We will return to this topic in the chapter on the kinetic theory of gases.

Substances	Specific Heat (c)	
<i>Solids</i>	J/kg · °C	kcal/kg · °C ^[2]
Aluminum	900	0.215
Asbestos	800	0.19
Concrete, granite (average)	840	0.20
Copper	387	0.0924
Glass	840	0.20
Gold	129	0.0308
Human body (average at 37 °C)	3500	0.83
Ice (average, −50 °C to 0 °C)	2090	0.50
Iron, steel	452	0.108
Lead	128	0.0305
Silver	235	0.0562
Wood	1700	0.40
<i>Liquids</i>		
Benzene	1740	0.415
Ethanol	2450	0.586
Glycerin	2410	0.576
Mercury	139	0.0333
Water (15.0 °C)	4186	1.000
<i>Gases</i> ^[3]		
Air (dry)	721 (1015)	0.172 (0.242)
Ammonia	1670 (2190)	0.399 (0.523)
Carbon dioxide	638 (833)	0.152 (0.199)
Nitrogen	739 (1040)	0.177 (0.248)

Substances	Specific Heat (<i>c</i>)	
Oxygen	651 (913)	0.156 (0.218)
Steam (100 °C)	1520 (2020)	0.363 (0.482)

Specific Heats of Various Substances^{[1][1]}The values for solids and liquids are at constant volume and 25 °C, except as noted. ^[2]These values are identical in units of cal/g · °C. ^[3]Specific heats at constant volume and at 20.0 °C except as noted, and at 1.00 atm pressure. Values in parentheses are specific heats at a constant pressure of 1.00 atm.

In general, specific heat also depends on temperature. Thus, a precise definition of *c* for a substance must be given in terms of an infinitesimal change in temperature. To do this, we note that $c = \frac{1}{m} \frac{\Delta Q}{\Delta T}$ and replace Δ with *d*:

Equation:

$$c = \frac{1}{m} \frac{dQ}{dT}.$$

Except for gases, the temperature and volume dependence of the specific heat of most substances is weak at normal temperatures. Therefore, we will generally take specific heats to be constant at the values given in the table.

Example:

Calculating the Required Heat

A 0.500-kg aluminum pan on a stove and 0.250 L of water in it are heated from 20.0 °C to 80.0 °C. (a) How much heat is required? What percentage of the heat is used to raise the temperature of (b) the pan and (c) the water?

Strategy

We can assume that the pan and the water are always at the same temperature. When you put the pan on the stove, the temperature of the water and that of the pan are increased by the same amount. We use the equation for the heat transfer for the given temperature change and mass of water and aluminum. The specific heat values for water and aluminum are given in [\[link\]](#).

Solution

1. Calculate the temperature difference:

Equation:

$$\Delta T = T_f - T_i = 60.0 \text{ °C}.$$

2. Calculate the mass of water. Because the density of water is 1000 kg/m³, 1 L of water has a mass of 1 kg, and the mass of 0.250 L of water is $m_w = 0.250$ kg.
3. Calculate the heat transferred to the water. Use the specific heat of water in [\[link\]](#):

Equation:

$$Q_w = m_w c_w \Delta T = (0.250 \text{ kg}) (4186 \text{ J/kg °C}) (60.0 \text{ °C}) = 62.8 \text{ kJ}.$$

4. Calculate the heat transferred to the aluminum. Use the specific heat for aluminum in [\[link\]](#):

Equation:

$$Q_{\text{Al}} = m_{\text{Al}} c_{\text{Al}} \Delta T = (0.500 \text{ kg}) (900 \text{ J/kg } ^\circ\text{C}) (60.0 ^\circ\text{C}) = 27.0 \text{ kJ}.$$

5. Find the total transferred heat:

Equation:

$$Q_{\text{Total}} = Q_{\text{W}} + Q_{\text{Al}} = 89.8 \text{ kJ}.$$

Significance

In this example, the heat transferred to the container is a significant fraction of the total transferred heat. Although the mass of the pan is twice that of the water, the specific heat of water is over four times that of aluminum. Therefore, it takes a bit more than twice as much heat to achieve the given temperature change for the water as for the aluminum pan.

[\[link\]](#) illustrates a temperature rise caused by doing work. (The result is the same as if the same amount of energy had been added with a blowtorch instead of mechanically.)

Example:

Calculating the Temperature Increase from the Work Done on a Substance

Truck brakes used to control speed on a downhill run do work, converting gravitational potential energy into increased internal energy (higher temperature) of the brake material ([\[link\]](#)). This conversion prevents the gravitational potential energy from being converted into kinetic energy of the truck. Since the mass of the truck is much greater than that of the brake material absorbing the energy, the temperature increase may occur too fast for sufficient heat to transfer from the brakes to the environment; in other words, the brakes may overheat.



The smoking brakes on a braking truck are visible evidence of the mechanical equivalent of heat.

Calculate the temperature increase of 10 kg of brake material with an average specific heat of $800 \text{ J/kg} \cdot ^\circ\text{C}$ if the material retains 10% of the energy from a 10,000-kg truck descending 75.0 m (in vertical displacement) at a constant speed.

Strategy

We calculate the gravitational potential energy (Mgh) that the entire truck loses in its descent, equate it to the increase in the brakes' internal energy, and then find the temperature increase produced in the brake material alone.

Solution

First we calculate the change in gravitational potential energy as the truck goes downhill:

Equation:

$$Mgh = (10,000 \text{ kg}) (9.80 \text{ m/s}^2) (75.0 \text{ m}) = 7.35 \times 10^6 \text{ J}.$$

Because the kinetic energy of the truck does not change, conservation of energy tells us the lost potential energy is dissipated, and we assume that 10% of it is transferred to internal energy of the brakes, so take $Q = Mgh/10$. Then we calculate the temperature change from the heat transferred, using

Equation:

$$\Delta T = \frac{Q}{mc},$$

where m is the mass of the brake material. Insert the given values to find

Equation:

$$\Delta T = \frac{7.35 \times 10^5 \text{ J}}{(10 \text{ kg})(800 \text{ J/kg} \cdot ^\circ\text{C})} = 92 ^\circ\text{C}.$$

Significance

If the truck had been traveling for some time, then just before the descent, the brake temperature would probably be higher than the ambient temperature. The temperature increase in the descent would likely raise the temperature of the brake material very high, so this technique is not practical. Instead, the truck would use the technique of engine braking. A different idea underlies the recent technology of hybrid and electric cars, where mechanical energy (kinetic and gravitational potential energy) is converted by the brakes into electrical energy in the battery, a process called regenerative braking.

In a common kind of problem, objects at different temperatures are placed in contact with each other but isolated from everything else, and they are allowed to come into equilibrium. A container that prevents heat transfer in or out is called a **calorimeter**, and the use of a calorimeter to make measurements (typically of heat or specific heat capacity) is called **calorimetry**.

We will use the term “calorimetry problem” to refer to any problem in which the objects concerned are thermally isolated from their surroundings. An important idea in solving calorimetry problems is that during a heat transfer between objects isolated from their surroundings, the heat gained by the colder object must equal the heat lost by the hotter object, due to conservation of energy:

Note:

Equation:

$$Q_{\text{cold}} + Q_{\text{hot}} = 0.$$

We express this idea by writing that the sum of the heats equals zero because the heat gained is usually considered positive; the heat lost, negative.

Example:

Calculating the Final Temperature in Calorimetry

Suppose you pour 0.250 kg of 20.0-°C water (about a cup) into a 0.500-kg aluminum pan off the stove with a temperature of 150 °C. Assume no heat transfer takes place to anything else: The pan is placed on an insulated pad, and heat transfer to the air is neglected in the short time needed to reach equilibrium. Thus, this is a calorimetry problem, even though no isolating container is specified. Also assume that a negligible amount of water boils off. What is the temperature when the water and pan reach thermal equilibrium?

Strategy

Originally, the pan and water are not in thermal equilibrium: The pan is at a higher temperature than the water. Heat transfer restores thermal equilibrium once the water and pan are in contact; it stops once thermal equilibrium between the pan and the water is achieved. The heat lost by the pan is equal to the heat gained by the water—that is the basic principle of calorimetry.

Solution

1. Use the equation for heat transfer $Q = mc\Delta T$ to express the heat lost by the aluminum pan in terms of the mass of the pan, the specific heat of aluminum, the initial temperature of the pan, and the final temperature:

Equation:

$$Q_{\text{hot}} = m_{\text{Al}}c_{\text{Al}}(T_{\text{f}} - 150\text{ }^{\circ}\text{C}).$$

2. Express the heat gained by the water in terms of the mass of the water, the specific heat of water, the initial temperature of the water, and the final temperature:

Equation:

$$Q_{\text{cold}} = m_{\text{w}}c_{\text{w}}(T_{\text{f}} - 20.0\text{ }^{\circ}\text{C}).$$

3. Note that $Q_{\text{hot}} < 0$ and $Q_{\text{cold}} > 0$ and that as stated above, they must sum to zero:

Equation:

$$\begin{aligned}Q_{\text{cold}} + Q_{\text{hot}} &= 0 \\Q_{\text{cold}} &= -Q_{\text{hot}} \\m_{\text{w}}c_{\text{w}}(T_{\text{f}} - 20.0\text{ }^{\circ}\text{C}) &= -m_{\text{Al}}c_{\text{Al}}(T_{\text{f}} - 150\text{ }^{\circ}\text{C}).\end{aligned}$$

4. This a linear equation for the unknown final temperature, T_{f} . Solving for T_{f} ,

Equation:

$$T_f = \frac{m_{A1}c_{A1}(150^\circ\text{C}) + m_w c_w(20.0^\circ\text{C})}{m_{A1}c_{A1} + m_w c_w},$$

and insert the numerical values:

Equation:

$$T_f = \frac{(0.500\text{ kg})(900\text{ J/kg}^\circ\text{C})(150^\circ\text{C}) + (0.250\text{ kg})(4186\text{ J/kg}^\circ\text{C})(20.0^\circ\text{C})}{(0.500\text{ kg})(900\text{ J/kg}^\circ\text{C}) + (0.250\text{ kg})(4186\text{ J/kg}^\circ\text{C})} = 59.1^\circ\text{C}.$$

Significance

Why is the final temperature so much closer to 20.0°C than to 150°C ? The reason is that water has a greater specific heat than most common substances and thus undergoes a smaller temperature change for a given heat transfer. A large body of water, such as a lake, requires a large amount of heat to increase its temperature appreciably. This explains why the temperature of a lake stays relatively constant during the day even when the temperature change of the air is large. However, the water temperature does change over longer times (e.g., summer to winter).

Note:

Exercise:

Problem:

Check Your Understanding If 25 kJ is necessary to raise the temperature of a rock from 25°C to 30°C , how much heat is necessary to heat the rock from 45°C to 50°C ?

Solution:

To a good approximation, the heat transfer depends only on the temperature difference. Since the temperature differences are the same in both cases, the same 25 kJ is necessary in the second case. (As we will see in the next section, the answer would have been different if the object had been made of some substance that changes phase anywhere between 30°C and 50°C .)

Example:

Temperature-Dependent Heat Capacity

At low temperatures, the specific heats of solids are typically proportional to T^3 . The first understanding of this behavior was due to the Dutch physicist Peter Debye, who in 1912, treated atomic oscillations with the quantum theory that Max Planck had recently used for radiation. For instance, a good approximation for the specific heat of salt, NaCl, is $c = 3.33 \times 10^4 \frac{\text{J}}{\text{kg}\cdot\text{K}} \left(\frac{T}{321\text{ K}}\right)^3$. The constant 321 K is called the *Debye temperature* of NaCl, Θ_D , and the formula works well when $T < 0.04\Theta_D$. Using this formula, how much heat is required to raise the temperature of 24.0 g of NaCl from 5 K to 15 K?

Solution

Because the heat capacity depends on the temperature, we need to use the equation

Equation:

$$c = \frac{1}{m} \frac{dQ}{dT}.$$

We solve this equation for Q by integrating both sides: $Q = m \int_{T_1}^{T_2} c dT$.

Then we substitute the given values in and evaluate the integral:

Equation:

$$Q = (0.024 \text{ kg}) \int_{T_1}^{T_2} 333 \times 10^4 \frac{\text{J}}{\text{kg} \cdot \text{K}} \left(\frac{T}{321 \text{ K}} \right)^3 dT = \left(6.04 \times 10^{-4} \frac{\text{J}}{\text{K}^4} \right) T^4 \bigg|_{5 \text{ K}}^{15 \text{ K}} = 30.2 \text{ J}.$$

Significance

If we had used the equation $Q = mc\Delta T$ and the room-temperature specific heat of salt, $880 \text{ J/kg} \cdot \text{K}$, we would have gotten a very different value.

Summary

- Heat and work are the two distinct methods of energy transfer.
- Heat transfer to an object when its temperature changes is often approximated well by $Q = mc\Delta T$, where m is the object's mass and c is the specific heat of the substance.

Conceptual Questions

Exercise:

Problem: How is heat transfer related to temperature?

Solution:

Temperature differences cause heat transfer.

Exercise:

Problem: Describe a situation in which heat transfer occurs.

Exercise:

Problem: When heat transfers into a system, is the energy stored as heat? Explain briefly.

Solution:

No, it is stored as thermal energy. A thermodynamic system does not have a well-defined quantity of heat.

Exercise:

Problem:

The brakes in a car increase in temperature by ΔT when bringing the car to rest from a speed v . How much greater would ΔT be if the car initially had twice the speed? You may assume the car stops fast enough that no heat transfers out of the brakes.

Problems**Exercise:****Problem:**

On a hot day, the temperature of an 80,000-L swimming pool increases by 1.50°C . What is the net heat transfer during this heating? Ignore any complications, such as loss of water by evaporation.

Solution:

$$m = 5.20 \times 10^8 \text{ J}$$

Exercise:**Problem:**

To sterilize a 50.0-g glass baby bottle, we must raise its temperature from 22.0°C to 95.0°C . How much heat transfer is required?

Exercise:**Problem:**

The same heat transfer into identical masses of different substances produces different temperature changes. Calculate the final temperature when 1.00 kcal of heat transfers into 1.00 kg of the following, originally at 20.0°C : (a) water; (b) concrete; (c) steel; and (d) mercury.

Solution:

$$Q = mc\Delta T \Rightarrow \Delta T = \frac{Q}{mc}; \text{ a. } 21.0^\circ\text{C}; \text{ b. } 25.0^\circ\text{C}; \text{ c. } 29.3^\circ\text{C}; \text{ d. } 50.0^\circ\text{C}$$

Exercise:**Problem:**

Rubbing your hands together warms them by converting work into thermal energy. If a woman rubs her hands back and forth for a total of 20 rubs, at a distance of 7.50 cm per rub, and with an average frictional force of 40.0 N, what is the temperature increase? The mass of tissues warmed is only 0.100 kg, mostly in the palms and fingers.

Exercise:**Problem:**

A 0.250-kg block of a pure material is heated from 20.0°C to 65.0°C by the addition of 4.35 kJ of energy. Calculate its specific heat and identify the substance of which it is most likely composed.

Solution:

$$Q = mc\Delta T \Rightarrow c = \frac{Q}{m\Delta T} = \frac{1.04 \text{ kcal}}{(0.250 \text{ kg})(45.0^\circ \text{C})} = 0.0924 \text{ kcal/kg} \cdot ^\circ \text{C}. \text{ It is copper.}$$

Exercise:**Problem:**

Suppose identical amounts of heat transfer into different masses of copper and water, causing identical changes in temperature. What is the ratio of the mass of copper to water?

Exercise:**Problem:**

(a) The number of kilocalories in food is determined by calorimetry techniques in which the food is burned and the amount of heat transfer is measured. How many kilocalories per gram are there in a 5.00-g peanut if the energy from burning it is transferred to 0.500 kg of water held in a 0.100-kg aluminum cup, causing a 54.9°C temperature increase? Assume the process takes place in an ideal calorimeter, in other words a perfectly insulated container. (b) Compare your answer to the following labeling information found on a package of dry roasted peanuts: a serving of 33 g contains 200 calories. Comment on whether the values are consistent.

Solution:

$$\begin{aligned} \text{a. } Q &= m_w c_w \Delta T + m_{A1} c_{A1} \Delta T = (m_w c_w + m_{A1} c_{A1}) \Delta T; \\ Q &= \left[(0.500 \text{ kg}) (1.00 \text{ kcal/kg} \cdot ^\circ \text{C}) + (0.100 \text{ kg}) (0.215 \text{ kcal/kg} \cdot ^\circ \text{C}) \right] (54.9^\circ \text{C}) = 28.63 \text{ kcal}; \\ \frac{Q}{m_p} &= \frac{28.63 \text{ kcal}}{5.00 \text{ g}} = 5.73 \text{ kcal/g}; \text{ b. } \frac{Q}{m_p} = \frac{200 \text{ kcal}}{33 \text{ g}} = 6 \text{ kcal/g, which is consistent with our} \\ &\text{results to part (a), to one significant figure.} \end{aligned}$$

Exercise:**Problem:**

Following vigorous exercise, the body temperature of an 80.0 kg person is 40.0°C . At what rate in watts must the person transfer thermal energy to reduce the body temperature to 37.0°C in 30.0 min, assuming the body continues to produce energy at the rate of 150 W? (1 watt = 1 joule/second or $1 \text{ W} = 1 \text{ J/s}$)

Exercise:**Problem:**

In a study of healthy young men^[footnote], doing 20 push-ups in 1 minute burned an amount of energy per kg that for a 70.0-kg man corresponds to 8.06 calories (kcal). How much would a 70.0-kg man's temperature rise if he did not lose any heat during that time?

JW Vezina, "An examination of the differences between two methods of estimating energy expenditure in resistance training activities," *Journal of Strength and Conditioning Research*, April 28, 2014, <http://www.ncbi.nlm.nih.gov/pubmed/24402448>

Solution:

0.139 °C

Exercise:

Problem:

A 1.28-kg sample of water at 10.0 °C is in a calorimeter. You drop a piece of steel with a mass of 0.385 kg at 215 °C into it. After the sizzling subsides, what is the final equilibrium temperature? (Make the reasonable assumptions that any steam produced condenses into liquid water during the process of equilibration and that the evaporation and condensation don't affect the outcome, as we'll see in the next section.)

Exercise:

Problem:

Repeat the preceding problem, assuming the water is in a glass beaker with a mass of 0.200 kg, which in turn is in a calorimeter. The beaker is initially at the same temperature as the water. Before doing the problem, should the answer be higher or lower than the preceding answer? Comparing the mass and specific heat of the beaker to those of the water, do you think the beaker will make much difference?

Solution:

It should be lower. The beaker will not make much difference: 16.3 °C

Glossary

calorie (cal)

energy needed to change the temperature of 1.00 g of water by 1.00 °C

calorimeter

container that prevents heat transfer in or out

calorimetry

study of heat transfer inside a container impervious to heat

heat

energy transferred solely due to a temperature difference

kilocalorie (kcal)

energy needed to change the temperature of 1.00 kg of water between 14.5 °C and 15.5 °C

mechanical equivalent of heat

work needed to produce the same effects as heat transfer

specific heat

amount of heat necessary to change the temperature of 1.00 kg of a substance by 1.00 °C; also called "specific heat capacity"

Phase Changes

By the end of this section, you will be able to:

- Describe phase transitions and equilibrium between phases
- Solve problems involving latent heat
- Solve calorimetry problems involving phase changes

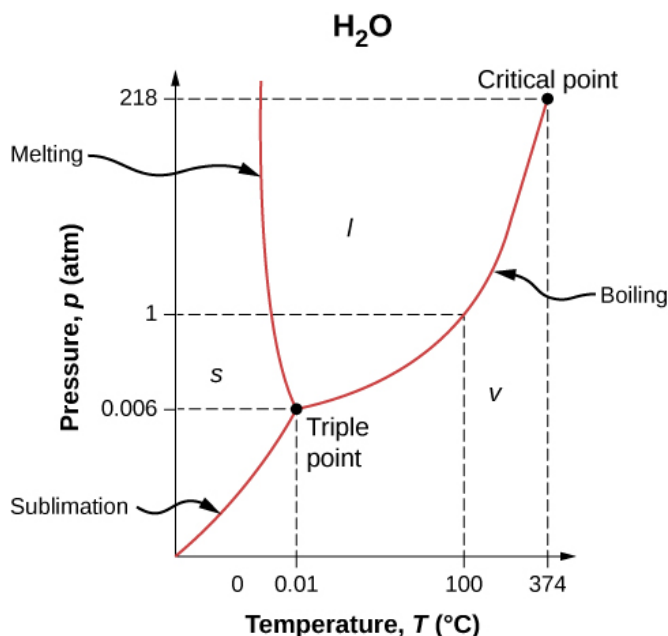
Phase transitions play an important theoretical and practical role in the study of heat flow. In melting (or “fusion”), a solid turns into a liquid; the opposite process is freezing. In evaporation, a liquid turns into a gas; the opposite process is condensation.

A substance melts or freezes at a temperature called its melting point, and boils (evaporates rapidly) or condenses at its boiling point. These temperatures depend on pressure. High pressure favors the denser form, so typically, high pressure raises the melting point and boiling point, and low pressure lowers them. For example, the boiling point of water is $100\text{ }^{\circ}\text{C}$ at 1.00 atm. At higher pressure, the boiling point is higher, and at lower pressure, it is lower. The main exception is the melting and freezing of water, discussed in the next section.

Phase Diagrams

The phase of a given substance depends on the pressure and temperature. Thus, plots of pressure versus temperature showing the phase in each region provide considerable insight into thermal properties of substances. Such a pT graph is called a **phase diagram**.

[\[link\]](#) shows the phase diagram for water. Using the graph, if you know the pressure and temperature, you can determine the phase of water. The solid curves—boundaries between phases—indicate phase transitions, that is, temperatures and pressures at which the phases coexist. For example, the boiling point of water is $100\text{ }^{\circ}\text{C}$ at 1.00 atm. As the pressure increases, the boiling temperature rises gradually to $374\text{ }^{\circ}\text{C}$ at a pressure of 218 atm. A pressure cooker (or even a covered pot) cooks food faster than an open pot, because the water can exist as a liquid at temperatures greater than $100\text{ }^{\circ}\text{C}$ without all boiling away. (As we’ll see in the next section, liquid water conducts heat better than steam or hot air.) The boiling point curve ends at a certain point called the **critical point**—that is, a **critical temperature**, above which the liquid and gas phases cannot be distinguished; the substance is called a *supercritical fluid*. At sufficiently high pressure above the critical point, the gas has the density of a liquid but does not condense. Carbon dioxide, for example, is supercritical at all temperatures above $31.0\text{ }^{\circ}\text{C}$. **Critical pressure** is the pressure of the critical point.



The phase diagram (pT graph) for water shows solid (s), liquid (l), and vapor (v) phases. At temperatures and pressure above those of the critical point, there is no distinction between liquid and vapor. Note that the axes are nonlinear and the graph is not to scale. This graph is simplified—it omits several exotic phases of ice at higher pressures. The phase diagram of water is unusual because the melting-point curve has a negative slope, showing that you can melt ice by *increasing* the pressure.

Similarly, the curve between the solid and liquid regions in [\[link\]](#) gives the melting temperature at various pressures. For example, the melting point is 0 °C at 1.00 atm, as expected. Water has the unusual property that ice is less dense than liquid water at the melting point, so at a fixed temperature, you can change the phase from solid (ice) to liquid (water) by increasing the pressure. That is, the melting temperature of ice falls with increased pressure, as the phase diagram shows. For example, when a car is driven over snow, the increased pressure from the tires melts the snowflakes; afterwards, the water refreezes and forms an ice layer.

As you learned in the earlier section on thermometers and temperature scales, the triple point is the combination of temperature and pressure at which ice, liquid water, and water vapor can coexist stably—that is, all three phases exist in equilibrium. For water, the triple point occurs at 273.16 K (0.01 °C) and 611.2 Pa; that is a more accurate calibration temperature than the melting point of water at 1.00 atm, or 273.15 K (0.0 °C).

Note:

View this [video](#) to see a substance at its triple point.

At pressures below that of the triple point, there is no liquid phase; the substance can exist as either gas or solid. For water, there is no liquid phase at pressures below 0.00600 atm. The phase change from solid to gas is called

sublimation. You may have noticed that snow can disappear into thin air without a trace of liquid water, or that ice cubes can disappear in a freezer. Both are examples of sublimation. The reverse also happens: Frost can form on very cold windows without going through the liquid stage. [\[link\]](#) shows the result, as well as showing a familiar example of sublimation. Carbon dioxide has no liquid phase at atmospheric pressure. Solid CO_2 is known as dry ice because instead of melting, it sublimates. Its sublimation temperature at atmospheric pressure is -78°C . Certain air fresheners use the sublimation of a solid to spread a perfume around a room. Some solids, such as osmium tetroxide, are so toxic that they must be kept in sealed containers to prevent human exposure to their sublimation-produced vapors.



(a)



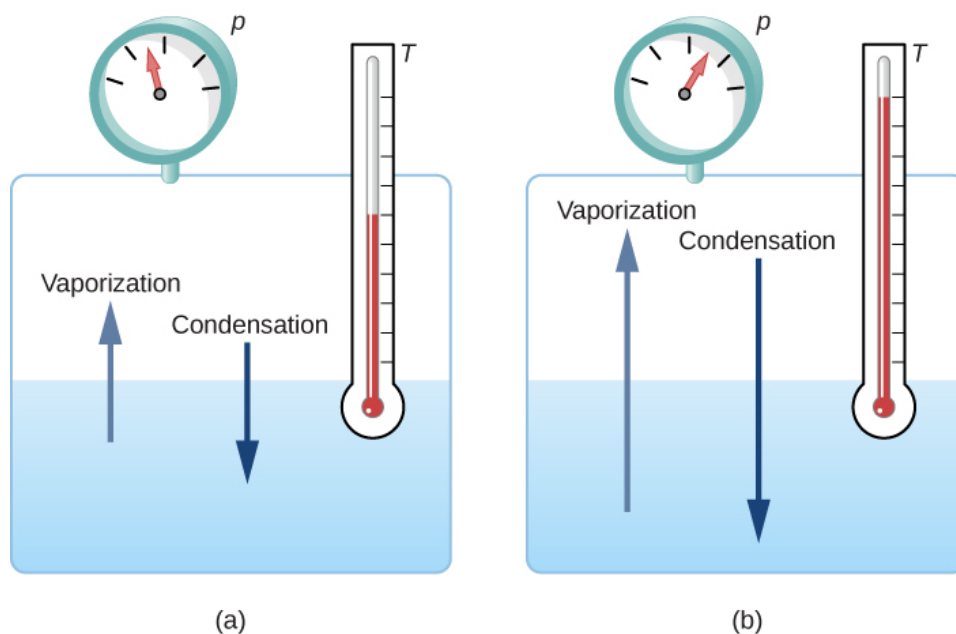
(b)

Direct transitions between solid and vapor are common, sometimes useful, and even beautiful. (a) Dry ice sublimates directly to carbon dioxide gas. The visible “smoke” consists of water droplets that condensed in the air cooled by the dry ice. (b) Frost forms patterns on a very cold window, an example of a solid formed directly from a vapor. (credit a: modification of work by Windell Oskay; credit b: modification of work by Liz West)

Equilibrium

At the melting temperature, the solid and liquid phases are in equilibrium. If heat is added, some of the solid will melt, and if heat is removed, some of the liquid will freeze. The situation is somewhat more complex for liquid-gas equilibrium. Generally, liquid and gas are in equilibrium at any temperature. We call the gas phase a **vapor** when it exists at a temperature below the boiling temperature, as it does for water at 20.0°C . Liquid in a closed container at a fixed temperature evaporates until the pressure of the gas reaches a certain value, called the **vapor pressure**, which depends on the gas and the temperature. At this equilibrium, if heat is added, some of the liquid will evaporate, and if heat is removed, some of the gas will condense; molecules either join the liquid or form suspended droplets. If there is not enough liquid for the gas to reach the vapor pressure in the container, all the liquid eventually evaporates.

If the vapor pressure of the liquid is greater than the *total* ambient pressure, including that of any air (or other gas), the liquid evaporates rapidly; in other words, it boils. Thus, the boiling point of a liquid at a given pressure is the temperature at which its vapor pressure equals the ambient pressure. Liquid and gas phases are in equilibrium at the boiling temperature ([\[link\]](#)). If a substance is in a closed container at the boiling point, then the liquid is boiling and the gas is condensing at the same rate without net change in their amounts.



Equilibrium between liquid and gas at two different boiling points inside a closed container. (a) The rates of boiling and condensation are equal at this combination of temperature and pressure, so the liquid and gas phases are in equilibrium. (b) At a higher temperature, the boiling rate is faster, that is, the rate at which molecules leave the liquid and enter the gas is faster. This increases the number of molecules in the gas, which increases the gas pressure, which in turn increases the rate at which gas molecules condense and enter the liquid. The pressure stops increasing when it reaches the point where the boiling rate and the condensation rate are equal. The gas and liquid are in equilibrium again at this higher temperature and pressure.

For water, $100\text{ }^{\circ}\text{C}$ is the boiling point at 1.00 atm , so water and steam should exist in equilibrium under these conditions. Why does an open pot of water at $100\text{ }^{\circ}\text{C}$ boil completely away? The gas surrounding an open pot is not pure water: it is mixed with air. If pure water and steam are in a closed container at $100\text{ }^{\circ}\text{C}$ and 1.00 atm , they will coexist—but with air over the pot, there are fewer water molecules to condense, and water boils away. Another way to see this is that at the boiling point, the vapor pressure equals the ambient pressure. However, part of the ambient pressure is due to air, so the pressure of the steam is less than the vapor pressure at that temperature, and evaporation continues. Incidentally, the equilibrium vapor pressure of solids is not zero, a fact that accounts for sublimation.

Note:

Exercise:

Problem:

Check Your Understanding Explain why a cup of water (or soda) with ice cubes stays at $0\text{ }^{\circ}\text{C}$, even on a hot summer day.

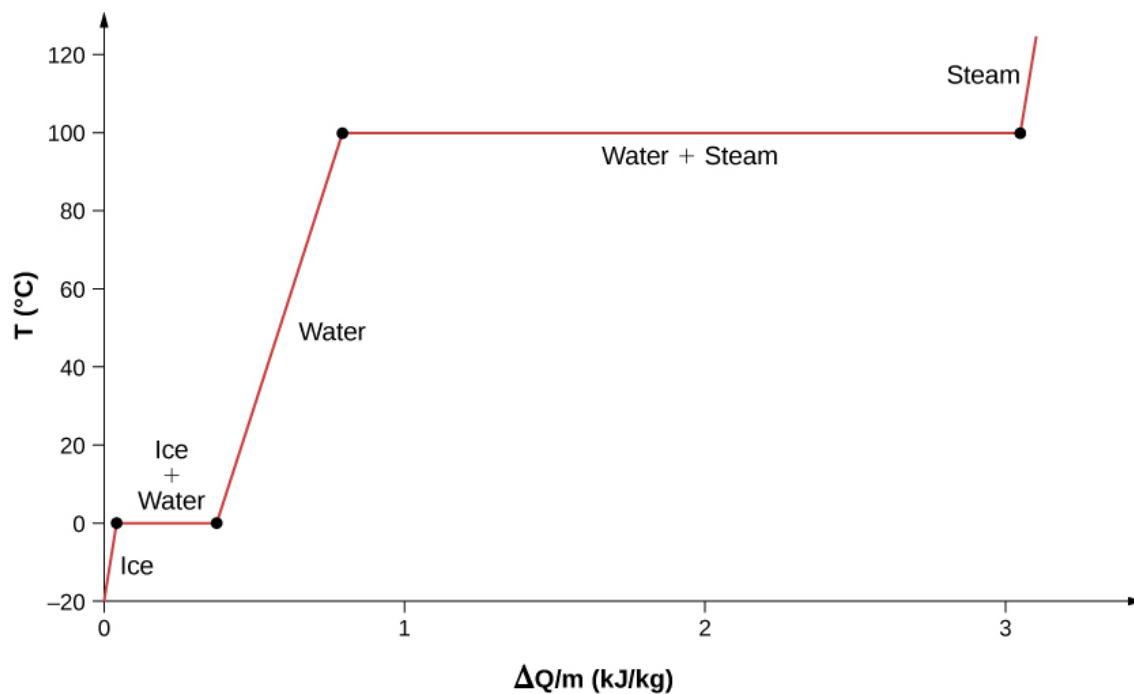
Solution:

The ice and liquid water are in thermal equilibrium, so that the temperature stays at the freezing temperature as long as ice remains in the liquid. (Once all of the ice melts, the water temperature will start to rise.)

Phase Change and Latent Heat

So far, we have discussed heat transfers that cause temperature change. However, in a phase transition, heat transfer does not cause any temperature change.

For an example of phase changes, consider the addition of heat to a sample of ice at $-20\text{ }^{\circ}\text{C}$ ([link](#)) and atmospheric pressure. The temperature of the ice rises linearly, absorbing heat at a constant rate of $2090\text{ J/kg} \cdot ^{\circ}\text{C}$ until it reaches $0\text{ }^{\circ}\text{C}$. Once at this temperature, the ice begins to melt and continues until it has all melted, absorbing 333 kJ/kg of heat. The temperature remains constant at $0\text{ }^{\circ}\text{C}$ during this phase change. Once all the ice has melted, the temperature of the liquid water rises, absorbing heat at a new constant rate of $4186\text{ J/kg} \cdot ^{\circ}\text{C}$. At $100\text{ }^{\circ}\text{C}$, the water begins to boil. The temperature again remains constant during this phase change while the water absorbs 2256 kJ/kg of heat and turns into steam. When all the liquid has become steam, the temperature rises again, absorbing heat at a rate of $2020\text{ J/kg} \cdot ^{\circ}\text{C}$. If we started with steam and cooled it to make it condense into liquid water and freeze into ice, the process would exactly reverse, with the temperature again constant during each phase transition.



Temperature versus heat. The system is constructed so that no vapor evaporates while ice warms to become liquid water, and so that, when vaporization occurs, the vapor remains in the system. The long stretches of constant temperatures at $0\text{ }^{\circ}\text{C}$ and $100\text{ }^{\circ}\text{C}$ reflect the large amounts of heat needed to cause melting and vaporization, respectively.

Where does the heat added during melting or boiling go, considering that the temperature does not change until the transition is complete? Energy is required to melt a solid, because the attractive forces between the molecules in the solid must be broken apart, so that in the liquid, the molecules can move around at comparable kinetic energies; thus, there is no rise in temperature. Energy is needed to vaporize a liquid for similar reasons. Conversely, work is done by attractive forces when molecules are brought together during freezing and condensation. That energy must be transferred out of the system, usually in the form of heat, to allow the molecules to stay together ([link](#)). Thus, condensation occurs in association with cold objects—the glass in [link](#), for example.



Condensation forms on this glass of iced tea because the temperature of the nearby air is reduced. The air cannot hold as much water as it did at room temperature, so water condenses. Energy is released when the water condenses, speeding the melting of the ice in the glass. (credit: Jenny Downing)

The energy released when a liquid freezes is used by orange growers when the temperature approaches 0°C . Growers spray water on the trees so that the water freezes and heat is released to the growing oranges. This prevents the temperature inside the orange from dropping below freezing, which would damage the fruit ([link](#)).



The ice on these trees released large amounts of energy when it froze, helping to prevent the temperature of the trees from dropping below 0°C . Water is intentionally sprayed on orchards to help prevent hard frosts. (credit: Hermann Hammer)

The energy involved in a phase change depends on the number of bonds or force pairs and their strength. The number of bonds is proportional to the number of molecules and thus to the mass of the sample. The energy per unit mass required to change a substance from the solid phase to the liquid phase, or released when the substance changes from liquid to solid, is known as the **heat of fusion**. The energy per unit mass required to change a substance from the liquid phase to the vapor phase is known as the **heat of vaporization**. The strength of the forces depends on the type of molecules. The heat Q absorbed or released in a phase change in a sample of mass m is given by

Note:

Equation:

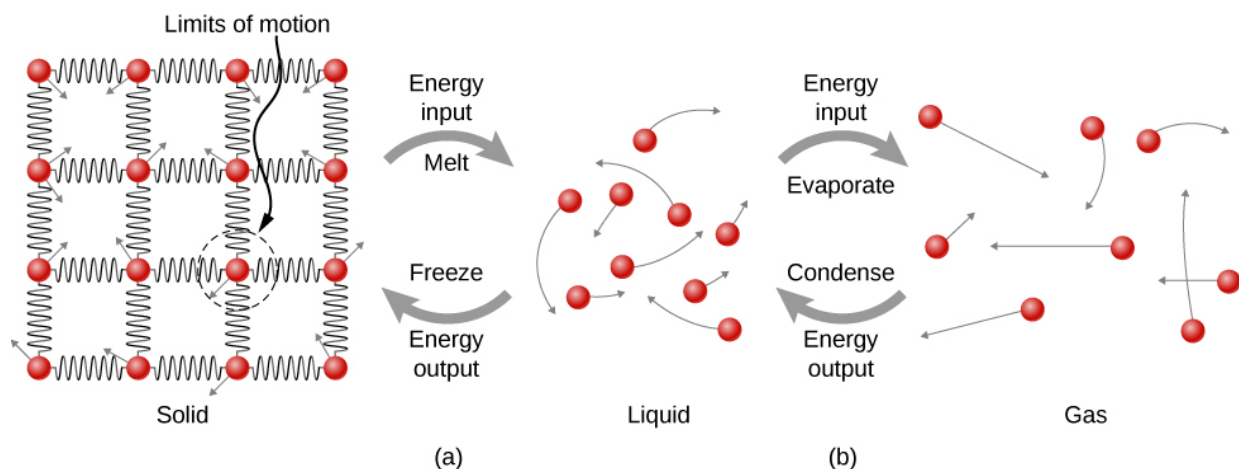
$$Q = mL_f(\text{melting/freezing})$$

Note:

Equation:

$$Q = mL_v(\text{vaporization/condensation})$$

where the latent heat of fusion L_f and latent heat of vaporization L_v are material constants that are determined experimentally. (Latent heats are also called **latent heat coefficients** and heats of transformation.) These constants are “latent,” or hidden, because in phase changes, energy enters or leaves a system without causing a temperature change in the system, so in effect, the energy is hidden.



(a) Energy is required to partially overcome the attractive forces (modeled as springs) between molecules in a solid to form a liquid. That same energy must be removed from the liquid for freezing to take place. (b)

Molecules become separated by large distances when going from liquid to vapor, requiring significant energy to completely overcome molecular attraction. The same energy must be removed from the vapor for condensation to take place.

[\[link\]](#) lists representative values of L_f and L_v in kJ/kg, together with melting and boiling points. Note that in general, $L_v > L_f$. The table shows that the amounts of energy involved in phase changes can easily be comparable to or greater than those involved in temperature changes, as [\[link\]](#) and the accompanying discussion also showed.

Substance	Melting Point (°C)	L_f		Boiling Point (°C)	L_v	
		kJ/kg	kcal/kg		kJ/kg	kcal/kg
Helium ^[2]	−272.2 (0.95 K)	5.23	1.25	−268.9 (4.2 K)	20.9	4.99
Hydrogen	−259.3 (13.9 K)	58.6	14.0	−252.9 (20.2 K)	452	108
Nitrogen	−210.0 (63.2 K)	25.5	6.09	−195.8 (77.4 K)	201	48.0
Oxygen	−218.8 (54.4 K)	13.8	3.30	−183.0 (90.2 K)	213	50.9
Ethanol	−114	104	24.9	78.3	854	204
Ammonia	−75	332	79.3	−33.4	1370	327
Mercury	−38.9	11.8	2.82	357	272	65.0
Water	0.00	334	79.8	100.0	2256 ^[3]	539 ^[4]

		L_f			L_v	
Sulfur	119	38.1	9.10	444.6	326	77.9
Lead	327	24.5	5.85	1750	871	208
Antimony	631	165	39.4	1440	561	134
Aluminum	660	380	90	2450	11400	2720
Silver	961	88.3	21.1	2193	2336	558
Gold	1063	64.5	15.4	2660	1578	377
Copper	1083	134	32.0	2595	5069	1211
Uranium	1133	84	20	3900	1900	454
Tungsten	3410	184	44	5900	4810	1150

Heats of Fusion and Vaporization^{[1][1]}Values quoted at the normal melting and boiling temperatures at standard atmospheric pressure (1 atm). ^[2]Helium has no solid phase at atmospheric pressure. The melting point given is at a pressure of 2.5 MPa. ^[3]At 37.0 °C (body temperature), the heat of vaporization L_v for water is 2430 kJ/kg or 580 kcal/kg. ^[4]At 37.0 °C (body temperature), the heat of vaporization, L_v for water is 2430 kJ/kg or 580 kcal/kg.

Phase changes can have a strong stabilizing effect on temperatures that are not near the melting and boiling points, since evaporation and condensation occur even at temperatures below the boiling point. For example, air temperatures in humid climates rarely go above approximately 38.0 °C because most heat transfer goes into evaporating water into the air. Similarly, temperatures in humid weather rarely fall below the dew point—the temperature where condensation occurs given the concentration of water vapor in the air—because so much heat is released when water vapor condenses.

More energy is required to evaporate water below the boiling point than at the boiling point, because the kinetic energy of water molecules at temperatures below 100 °C is less than that at 100 °C, so less energy is available from random thermal motions. For example, at body temperature, evaporation of sweat from the skin requires a heat input of 2428 kJ/kg, which is about 10% higher than the latent heat of vaporization at 100 °C. This heat comes from the skin, and this evaporative cooling effect of sweating helps reduce the body temperature in hot weather. However, high humidity inhibits evaporation, so that body temperature might rise, while unevaporated sweat might be left on your brow.

Example:

Calculating Final Temperature from Phase Change

Three ice cubes are used to chill a soda at 20 °C with mass $m_{\text{soda}} = 0.25$ kg. The ice is at 0 °C and each ice cube has a mass of 6.0 g. Assume that the soda is kept in a foam container so that heat loss can be ignored and that the soda has the same specific heat as water. Find the final temperature when all ice has melted.

Strategy

The ice cubes are at the melting temperature of 0 °C. Heat is transferred from the soda to the ice for melting. Melting yields water at 0 °C, so more heat is transferred from the soda to this water until the water plus soda system reaches thermal equilibrium.

The heat transferred to the ice is

Equation:

$$Q_{\text{ice}} = m_{\text{ice}}L_f + m_{\text{ice}}c_W (T_f - 0^\circ\text{C}).$$

The heat given off by the soda is

Equation:

$$Q_{\text{soda}} = m_{\text{soda}}c_W (T_f - 20^\circ\text{C}).$$

Since no heat is lost, $Q_{\text{ice}} = -Q_{\text{soda}}$, as in [\[link\]](#), so that

Equation:

$$m_{\text{ice}}L_f + m_{\text{ice}}c_W (T_f - 0^\circ\text{C}) = -m_{\text{soda}}c_W (T_f - 20^\circ\text{C}).$$

Solve for the unknown quantity T_f :

Equation:

$$T_f = \frac{m_{\text{soda}}c_W (20^\circ\text{C}) - m_{\text{ice}}L_f}{(m_{\text{soda}} + m_{\text{ice}})c_W}.$$

Solution

First we identify the known quantities. The mass of ice is $m_{\text{ice}} = 3 \times 6.0 \text{ g} = 0.018 \text{ kg}$ and the mass of soda is $m_{\text{soda}} = 0.25 \text{ kg}$. Then we calculate the final temperature:

Equation:

$$T_f = \frac{20,930 \text{ J} - 6012 \text{ J}}{1122 \text{ J}/^\circ\text{C}} = 13^\circ\text{C}.$$

Significance

This example illustrates the large energies involved during a phase change. The mass of ice is about 7% of the mass of the soda but leads to a noticeable change in the temperature of the soda. Although we assumed that the ice was at the freezing temperature, this is unrealistic for ice straight out of a freezer: The typical temperature is -6°C . However, this correction makes no significant change from the result we found. Can you explain why?

Like solid-liquid and liquid-vapor transitions, direct solid-vapor transitions or sublimations involve heat. The energy transferred is given by the equation $Q = mL_s$, where L_s is the **heat of sublimation**, analogous to L_f and L_v . The heat of sublimation at a given temperature is equal to the heat of fusion plus the heat of vaporization at that temperature.

We can now calculate a number of effects related to temperature and phase change. In each case, it is necessary to identify which temperature and phase changes are taking place. Keep in mind that heat transfer and work can cause both temperature and phase changes.

Note:

Problem-Solving Strategy: The Effects of Heat Transfer

1. Examine the situation to determine that there is a change in the temperature or phase. Is there heat transfer into or out of the system? When it is not obvious whether a phase change occurs or not, you may wish to first solve the problem as if there were no phase changes, and examine the temperature change obtained. If it is sufficient to take you past a boiling or melting point, you should then go back and do the problem in steps—temperature change, phase change, subsequent temperature change, and so on.
2. Identify and list all objects that change temperature or phase.
3. Identify exactly what needs to be determined in the problem (identify the unknowns). A written list is useful.

4. Make a list of what is given or what can be inferred from the problem as stated (identify the knowns). If there is a temperature change, the transferred heat depends on the specific heat of the substance ([Heat Transfer, Specific Heat, and Calorimetry](#)), and if there is a phase change, the transferred heat depends on the latent heat of the substance ([link](#)).
5. Solve the appropriate equation for the quantity to be determined (the unknown).
6. Substitute the knowns along with their units into the appropriate equation and obtain numerical solutions complete with units. You may need to do this in steps if there is more than one state to the process, such as a temperature change followed by a phase change. However, in a calorimetry problem, each step corresponds to a term in the single equation $Q_{\text{hot}} + Q_{\text{cold}} = 0$.
7. Check the answer to see if it is reasonable. Does it make sense? As an example, be certain that any temperature change does not also cause a phase change that you have not taken into account.

Note:

Exercise:

Problem:

Check Your Understanding Why does snow often remain even when daytime temperatures are higher than the freezing temperature?

Solution:

Snow is formed from ice crystals and thus is the solid phase of water. Because enormous heat is necessary for phase changes, it takes a certain amount of time for this heat to be transferred from the air, even if the air is above 0°C .

Summary

- Most substances have three distinct phases (under ordinary conditions on Earth), and they depend on temperature and pressure.
- Two phases coexist (i.e., they are in thermal equilibrium) at a set of pressures and temperatures.
- Phase changes occur at fixed temperatures for a given substance at a given pressure, and these temperatures are called boiling, freezing (or melting), and sublimation points.

Conceptual Questions

Exercise:

Problem:

A pressure cooker contains water and steam in equilibrium at a pressure greater than atmospheric pressure. How does this greater pressure increase cooking speed?

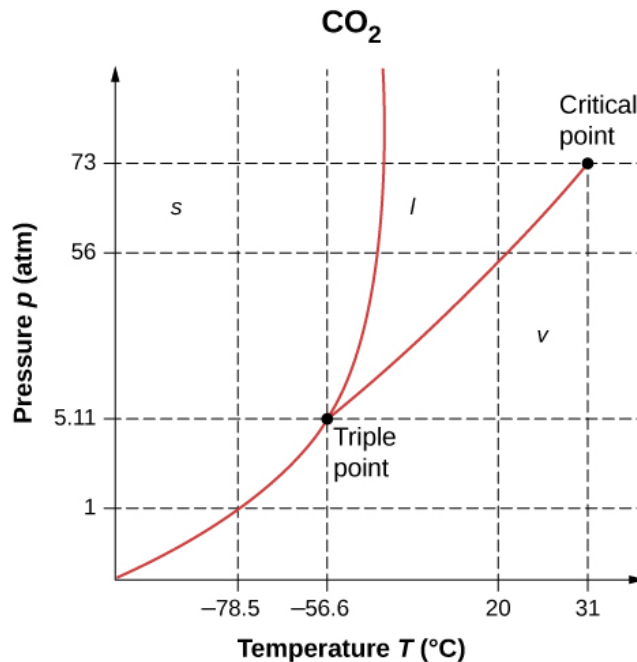
Solution:

It raises the boiling point, so the water, which the food gains heat from, is at a higher temperature.

Exercise:

Problem:

As shown below, which is the phase diagram for carbon dioxide, what is the vapor pressure of solid carbon dioxide (dry ice) at $-78.5\text{ }^{\circ}\text{C}$? (Note that the axes in the figure are nonlinear and the graph is not to scale.)



Exercise:

Problem:

Can carbon dioxide be liquefied at room temperature ($20\text{ }^{\circ}\text{C}$)? If so, how? If not, why not? (See the phase diagram in the preceding problem.)

Solution:

Yes, by raising the pressure above 56 atm.

Exercise:

Problem: What is the distinction between gas and vapor?

Exercise:

Problem: Heat transfer can cause temperature and phase changes. What else can cause these changes?

Solution:

work

Exercise:

Problem:

How does the latent heat of fusion of water help slow the decrease of air temperatures, perhaps preventing temperatures from falling significantly below $0\text{ }^{\circ}\text{C}$, in the vicinity of large bodies of water?

Exercise:

Problem: What is the temperature of ice right after it is formed by freezing water?

Solution:

0 °C (at or near atmospheric pressure)

Exercise:

Problem:

If you place 0 °C ice into 0 °C water in an insulated container, what will the net result be? Will there be less ice and more liquid water, or more ice and less liquid water, or will the amounts stay the same?

Exercise:

Problem:

What effect does condensation on a glass of ice water have on the rate at which the ice melts? Will the condensation speed up the melting process or slow it down?

Solution:

Condensation releases heat, so it speeds up the melting.

Exercise:

Problem:

In Miami, Florida, which has a very humid climate and numerous bodies of water nearby, it is unusual for temperatures to rise above about 38 °C (100 °F). In the desert climate of Phoenix, Arizona, however, temperatures rise above that almost every day in July and August. Explain how the evaporation of water helps limit high temperatures in humid climates.

Exercise:

Problem:

In winter, it is often warmer in San Francisco than in Sacramento, 150 km inland. In summer, it is nearly always hotter in Sacramento. Explain how the bodies of water surrounding San Francisco moderate its extreme temperatures.

Solution:

Because of water's high specific heat, it changes temperature less than land. Also, evaporation reduces temperature rises. The air tends to stay close to equilibrium with the water, so its temperature does not change much where there's a lot of water around, as in San Francisco but not Sacramento.

Exercise:

Problem:

Freeze-dried foods have been dehydrated in a vacuum. During the process, the food freezes and must be heated to facilitate dehydration. Explain both how the vacuum speeds up dehydration and why the food freezes as a result.

Exercise:

Problem:

In a physics classroom demonstration, an instructor inflates a balloon by mouth and then cools it in liquid nitrogen. When cold, the shrunken balloon has a small amount of light blue liquid in it, as well as some snow-like crystals. As it warms up, the liquid boils, and part of the crystals sublime, with some crystals lingering for a while and then producing a liquid. Identify the blue liquid and the two solids in the cold balloon. Justify your identifications using data from [\[link\]](#).

Solution:

The liquid is oxygen, whose boiling point is above that of nitrogen but whose melting point is below the boiling point of liquid nitrogen. The crystals that sublime are carbon dioxide, which has no liquid phase at atmospheric pressure. The crystals that melt are water, whose melting point is above carbon dioxide's sublimation point. The water came from the instructor's breath.

Problems**Exercise:****Problem:**

How much heat transfer (in kilocalories) is required to thaw a 0.450-kg package of frozen vegetables originally at 0°C if their heat of fusion is the same as that of water?

Exercise:**Problem:**

A bag containing 0°C ice is much more effective in absorbing energy than one containing the same amount of 0°C water. (a) How much heat transfer is necessary to raise the temperature of 0.800 kg of water from 0°C to 30.0°C ? (b) How much heat transfer is required to first melt 0.800 kg of 0°C ice and then raise its temperature? (c) Explain how your answer supports the contention that the ice is more effective.

Solution:

a. $1.00 \times 10^5 \text{ J}$; b. $3.68 \times 10^5 \text{ J}$; c. The ice is much more effective in absorbing heat because it first must be melted, which requires a lot of energy, and then it gains the same amount of heat as the bag that started with water. The first $2.67 \times 10^5 \text{ J}$ of heat is used to melt the ice, then it absorbs the $1.00 \times 10^5 \text{ J}$ of heat as water.

Exercise:**Problem:**

(a) How much heat transfer is required to raise the temperature of a 0.750-kg aluminum pot containing 2.50 kg of water from 30.0°C to the boiling point and then boil away 0.750 kg of water? (b) How long does this take if the rate of heat transfer is 500 W?

Exercise:**Problem:**

Condensation on a glass of ice water causes the ice to melt faster than it would otherwise. If 8.00 g of vapor condense on a glass containing both water and 200 g of ice, how many grams of the ice will melt as a result? Assume no other heat transfer occurs. Use L_v for water at 37°C as a better approximation than L_v for water at 100°C .)

Solution:

58.1 g

Exercise:**Problem:**

On a trip, you notice that a 3.50-kg bag of ice lasts an average of one day in your cooler. What is the average power in watts entering the ice if it starts at 0 °C and completely melts to 0 °C water in exactly one day?

Exercise:**Problem:**

On a certain dry sunny day, a swimming pool's temperature would rise by 1.50 °C if not for evaporation. What fraction of the water must evaporate to carry away precisely enough energy to keep the temperature constant?

Solution:

Let M be the mass of pool water and m be the mass of pool water that evaporates.

$$Mc\Delta T = mL_{V(37^\circ\text{C})} \Rightarrow \frac{m}{M} = \frac{c\Delta T}{L_{V(37^\circ\text{C})}} = \frac{(1.00 \text{ kcal/kg}\cdot^\circ\text{C})(1.50^\circ\text{C})}{580 \text{ kcal/kg}} = 2.59 \times 10^{-3};$$

(Note that L_V for water at 37 °C is used here as a better approximation than L_V for 100 °C water.)

Exercise:**Problem:**

(a) How much heat transfer is necessary to raise the temperature of a 0.200-kg piece of ice from -20.0°C to 130.0°C , including the energy needed for phase changes? (b) How much time is required for each stage, assuming a constant 20.0 kJ/s rate of heat transfer? (c) Make a graph of temperature versus time for this process.

Exercise:**Problem:**

In 1986, an enormous iceberg broke away from the Ross Ice Shelf in Antarctica. It was an approximately rectangular prism 160 km long, 40.0 km wide, and 250 m thick. (a) What is the mass of this iceberg, given that the density of ice is 917 kg/m³? (b) How much heat transfer (in joules) is needed to melt it? (c) How many years would it take sunlight alone to melt ice this thick, if the ice absorbs an average of 100 W/m², 12.00 h per day?

Solution:

a. 1.47×10^{15} kg; b. 4.90×10^{20} J; c. 48.5 y

Exercise:**Problem:**

How many grams of coffee must evaporate from 350 g of coffee in a 100-g glass cup to cool the coffee and the cup from 95.0 °C to 45.0 °C? Assume the coffee has the same thermal properties as water and that the average heat of vaporization is 2340 kJ/kg (560 kcal/g). Neglect heat losses through processes other than evaporation, as well as the change in mass of the coffee as it cools. Do the latter two assumptions cause your answer to be higher or lower than the true answer?

Exercise:

Problem:

(a) It is difficult to extinguish a fire on a crude oil tanker, because each liter of crude oil releases 2.80×10^7 J of energy when burned. To illustrate this difficulty, calculate the number of liters of water that must be expended to absorb the energy released by burning 1.00 L of crude oil, if the water's temperature rises from 20.0°C to 100°C , it boils, and the resulting steam's temperature rises to 300°C at constant pressure. (b) Discuss additional complications caused by the fact that crude oil is less dense than water.

Solution:

a. 9.67 L; b. Crude oil is less dense than water, so it floats on top of the water, thereby exposing it to the oxygen in the air, which it uses to burn. Also, if the water is under the oil, it is less able to absorb the heat generated by the oil.

Exercise:**Problem:**

The energy released from condensation in thunderstorms can be very large. Calculate the energy released into the atmosphere for a small storm of radius 1 km, assuming that 1.0 cm of rain is precipitated uniformly over this area.

Exercise:**Problem:**

To help prevent frost damage, 4.00 kg of water at 0°C is sprayed onto a fruit tree. (a) How much heat transfer occurs as the water freezes? (b) How much would the temperature of the 200-kg tree decrease if this amount of heat transferred from the tree? Take the specific heat to be $3.35\text{ kJ/kg} \cdot ^\circ\text{C}$, and assume that no phase change occurs in the tree.

Solution:

a. 319 kcal; b. 2.00°C

Exercise:**Problem:**

A 0.250-kg aluminum bowl holding 0.800 kg of soup at 25.0°C is placed in a freezer. What is the final temperature if 388 kJ of energy is transferred from the bowl and soup, assuming the soup's thermal properties are the same as that of water?

Exercise:**Problem:**

A 0.0500-kg ice cube at -30.0°C is placed in 0.400 kg of 35.0°C water in a very well-insulated container. What is the final temperature?

Solution:

First bring the ice up to 0°C and melt it with heat $Q_1 : 4.74\text{ kcal}$. This lowers the temperature of water by $\Delta T_2 : 23.15^\circ\text{C}$. Now, the heat lost by the hot water equals that gained by the cold water (T_f is the final temperature): 20.6°C

Exercise:

Problem:

If you pour 0.0100 kg of 20.0 °C water onto a 1.20-kg block of ice (which is initially at −15.0 °C), what is the final temperature? You may assume that the water cools so rapidly that effects of the surroundings are negligible.

Exercise:**Problem:**

Indigenous people sometimes cook in watertight baskets by placing hot rocks into water to bring it to a boil. What mass of 500-°C granite must be placed in 4.00 kg of 15.0-°C water to bring its temperature to 100 °C, if 0.0250 kg of water escapes as vapor from the initial sizzle? You may neglect the effects of the surroundings.

Solution:

Let the subscripts r, e, v, and w represent rock, equilibrium, vapor, and water, respectively.

$$m_r c_r (T_1 - T_e) = m_v L_v + m_w c_w (T_e - T_2);$$

$$\begin{aligned} m_r &= \frac{m_v L_v + m_w c_w (T_e - T_2)}{c_r (T_1 - T_e)} \\ &= \frac{(0.0250 \text{ kg})(2256 \times 10^3 \text{ J/kg}) + (3.975 \text{ kg})(4186 \times 10^3 \text{ J/kg} \cdot ^\circ\text{C})(100^\circ\text{C} - 15^\circ\text{C})}{(840 \text{ J/kg} \cdot ^\circ\text{C})(500^\circ\text{C} - 100^\circ\text{C})} \\ &= 4.38 \text{ kg} \end{aligned}$$

Exercise:**Problem:**

What would the final temperature of the pan and water be in [\[link\]](#) if 0.260 kg of water were placed in the pan and 0.0100 kg of the water evaporated immediately, leaving the remainder to come to a common temperature with the pan?

Glossary

critical point

for a given substance, the combination of temperature and pressure above which the liquid and gas phases are indistinguishable

critical pressure

pressure at the critical point

critical temperature

temperature at the critical point

heat of fusion

energy per unit mass required to change a substance from the solid phase to the liquid phase, or released when the substance changes from liquid to solid

heat of sublimation

energy per unit mass required to change a substance from the solid phase to the vapor phase

heat of vaporization

energy per unit mass required to change a substance from the liquid phase to the vapor phase

latent heat coefficient

general term for the heats of fusion, vaporization, and sublimation

phase diagram

graph of pressure vs. temperature of a particular substance, showing at which pressures and temperatures the phases of the substance occur

sublimation

phase change from solid to gas

vapor

gas at a temperature below the boiling temperature

vapor pressure

pressure at which a gas coexists with its solid or liquid phase

Mechanisms of Heat Transfer

By the end of this section, you will be able to:

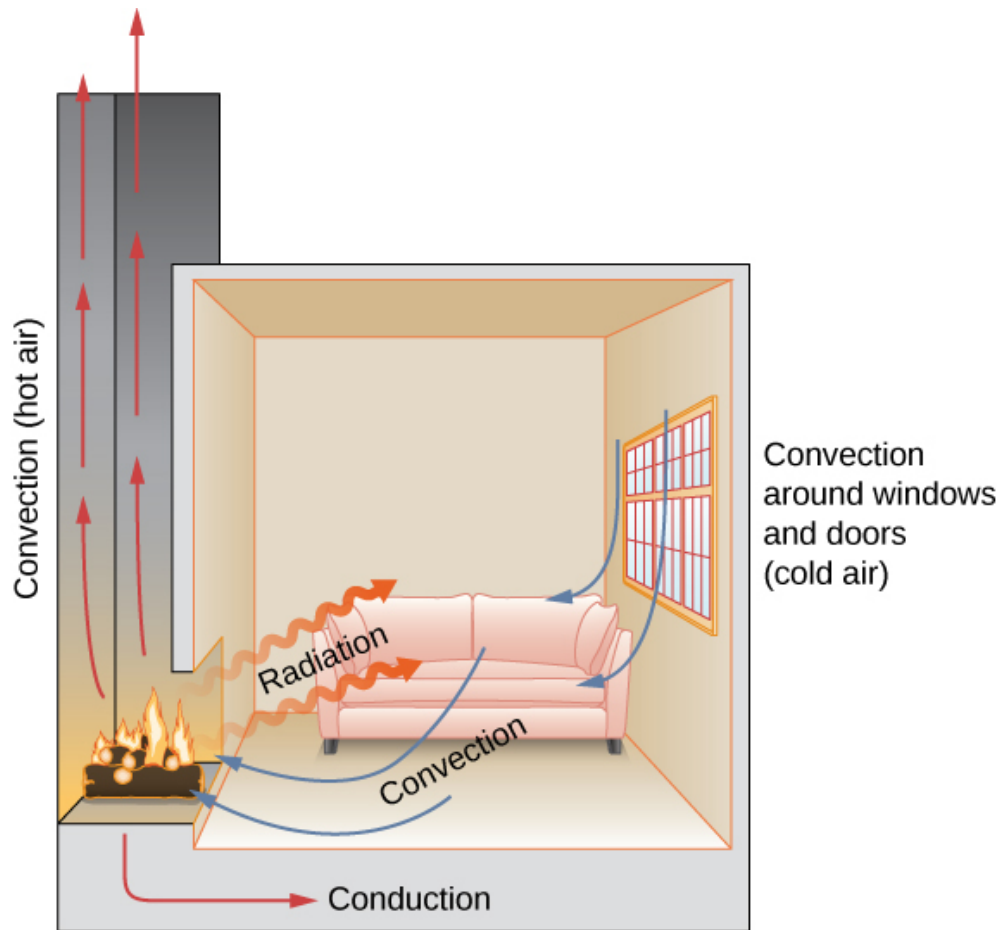
- Explain some phenomena that involve conductive, convective, and radiative heat transfer
- Solve problems on the relationships between heat transfer, time, and rate of heat transfer
- Solve problems using the formulas for conduction and radiation

Just as interesting as the effects of heat transfer on a system are the methods by which it occurs. Whenever there is a temperature difference, heat transfer occurs. It may occur rapidly, as through a cooking pan, or slowly, as through the walls of a picnic ice chest. So many processes involve heat transfer that it is hard to imagine a situation where no heat transfer occurs. Yet every heat transfer takes place by only three methods:

1. **Conduction** is heat transfer through stationary matter by physical contact. (The matter is stationary on a macroscopic scale—we know that thermal motion of the atoms and molecules occurs at any temperature above absolute zero.) Heat transferred from the burner of a stove through the bottom of a pan to food in the pan is transferred by conduction.
2. **Convection** is the heat transfer by the macroscopic movement of a fluid. This type of transfer takes place in a forced-air furnace and in weather systems, for example.
3. Heat transfer by **radiation** occurs when microwaves, infrared radiation, visible light, or another form of electromagnetic radiation is emitted or absorbed. An obvious example is the warming of Earth by the Sun. A less obvious example is thermal radiation from the human body.

In the illustration at the beginning of this chapter, the fire warms the snowshoers' faces largely by radiation. Convection carries some heat to them, but most of the air flow from the fire is upward (creating the familiar shape of flames), carrying heat to the food being cooked and into the sky. The snowshoers wear clothes designed with low conductivity to prevent heat flow out of their bodies.

In this section, we examine these methods in some detail. Each method has unique and interesting characteristics, but all three have two things in common: They transfer heat solely because of a temperature difference, and the greater the temperature difference, the faster the heat transfer ([link](#)).



In a fireplace, heat transfer occurs by all three methods: conduction, convection, and radiation. Radiation is responsible for most of the heat transferred into the room. Heat transfer also occurs through conduction into the room, but much slower. Heat transfer by convection also occurs through cold air entering the room around windows and hot air leaving the room by rising up the chimney.

Note:

Exercise:

Problem:

Check Your Understanding Name an example from daily life (different from the text) for each mechanism of heat transfer.

Solution:

Conduction: Heat transfers into your hands as you hold a hot cup of coffee.

Convection: Heat transfers as the barista “steams” cold milk to make hot cocoa.

Radiation: Heat transfers from the Sun to a jar of water with tea leaves in it to make “Sun tea.” A great many other answers are possible.

Conduction

As you walk barefoot across the living room carpet in a cold house and then step onto the kitchen tile floor, your feet feel colder on the tile. This result is intriguing, since the carpet and tile floor are both at the same temperature. The different sensation is explained by the different rates of heat transfer: The heat loss is faster for skin in contact with the tiles than with the carpet, so the sensation of cold is more intense.

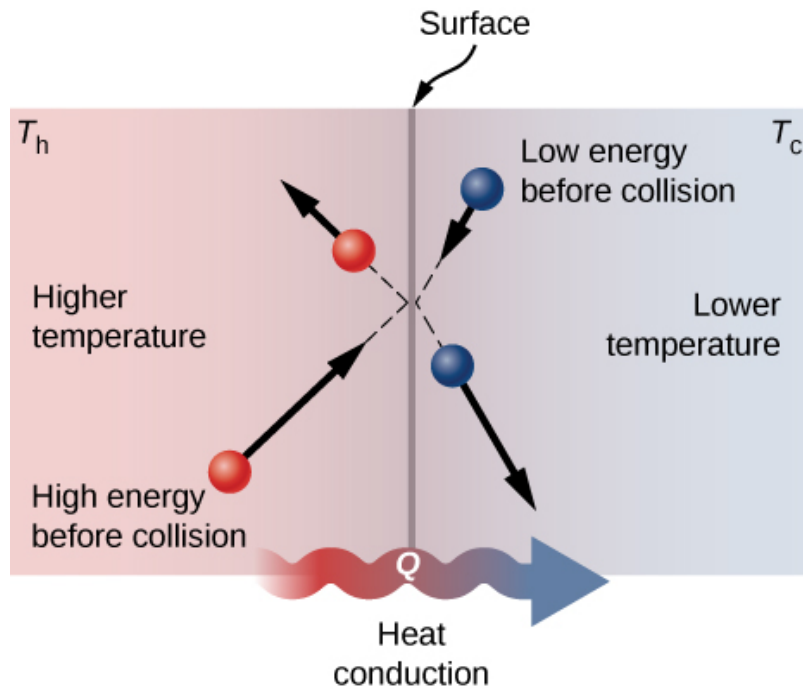
Some materials conduct thermal energy faster than others. [\[link\]](#) shows a material that conducts heat slowly—it is a good thermal insulator, or poor heat conductor—used to reduce heat flow into and out of a house.



Insulation is used to limit the conduction of heat from the inside to the outside (in winter) and from the outside to the inside (in summer). (credit: Giles Douglas)

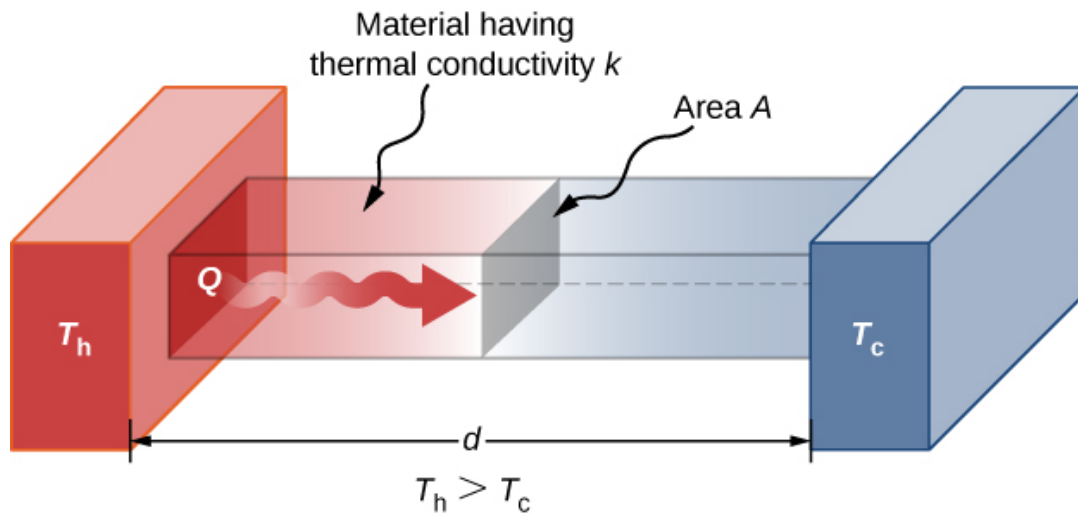
A molecular picture of heat conduction will help justify the equation that describes it. [\[link\]](#) shows molecules in two bodies at different temperatures, T_h and T_c , for “hot” and “cold.” The average kinetic energy of a molecule in the hot body is higher than in the colder body. If two molecules collide, energy transfers from the high-energy to the low-energy molecule. In a metal, the picture would also include free valence electrons colliding with each other and with atoms, likewise transferring energy. The cumulative effect of all collisions is a net flux of heat from the hotter body to the colder body. Thus, the rate of heat transfer increases with increasing temperature difference $\Delta T = T_h - T_c$. If the temperatures are the same, the net heat transfer rate is zero.

Because the number of collisions increases with increasing area, heat conduction is proportional to the cross-sectional area—a second factor in the equation.



Molecules in two bodies at different temperatures have different average kinetic energies. Collisions occurring at the contact surface tend to transfer energy from high-temperature regions to low-temperature regions. In this illustration, a molecule in the lower-temperature region (right side) has low energy before collision, but its energy increases after colliding with a high-energy molecule at the contact surface. In contrast, a molecule in the higher-temperature region (left side) has high energy before collision, but its energy decreases after colliding with a low-energy molecule at the contact surface.

A third quantity that affects the conduction rate is the thickness of the material through which heat transfers. [\[link\]](#) shows a slab of material with a higher temperature on the left than on the right. Heat transfers from the left to the right by a series of molecular collisions. The greater the distance between hot and cold, the more time the material takes to transfer the same amount of heat.



Heat conduction occurs through any material, represented here by a rectangular bar, whether window glass or walrus blubber.

All four of these quantities appear in a simple equation deduced from and confirmed by experiments. The **rate of conductive heat transfer** through a slab of material, such as the one in [\[link\]](#), is given by

Note:

Equation:

$$P = \frac{dQ}{dT} = \frac{kA(T_h - T_c)}{d}$$

where P is the power or rate of heat transfer in watts or in kilocalories per second, A and d are its surface area and thickness, as shown in [\[link\]](#), $T_h - T_c$ is the temperature difference across the slab, and k is the **thermal conductivity** of the material. [\[link\]](#) gives representative values of thermal conductivity.

More generally, we can write

Equation:

$$P = -kA \frac{dT}{dx},$$

where x is the coordinate in the direction of heat flow. Since in [\[link\]](#), the power and area are constant, dT/dx is constant, and the temperature decreases linearly from T_h to T_c .

Substance	Thermal Conductivity k (W/m · °C)
Diamond	2000
Silver	420
Copper	390
Gold	318
Aluminum	220
Steel iron	80
Steel (stainless)	14
Ice	2.2
Glass (average)	0.84
Concrete brick	0.84
Water	0.6
Fatty tissue (without blood)	0.2
Asbestos	0.16
Plasterboard	0.16
Wood	0.08–0.16
Snow (dry)	0.10

Substance	Thermal Conductivity k (W/m · °C)
Cork	0.042
Glass wool	0.042
Wool	0.04
Down feathers	0.025
Air	0.023
Polystyrene foam	0.010

Thermal Conductivities of Common Substances Values are given for temperatures near 0 °C.

Example:

Calculating Heat Transfer through Conduction

A polystyrene foam icebox has a total area of 0.950 m² and walls with an average thickness of 2.50 cm. The box contains ice, water, and canned beverages at 0 °C. The inside of the box is kept cold by melting ice. How much ice melts in one day if the icebox is kept in the trunk of a car at 35.0 °C?

Strategy

This question involves both heat for a phase change (melting of ice) and the transfer of heat by conduction. To find the amount of ice melted, we must find the net heat transferred. This value can be obtained by calculating the rate of heat transfer by conduction and multiplying by time.

Solution

First we identify the knowns.

$k = 0.010$ W/m · °C for polystyrene foam; $A = 0.950$ m²;

$d = 2.50$ cm = 0.0250 m;; $T_c = 0$ °C; $T_h = 35.0$ °C;

$t = 1$ day = 24 hours - 84,400 s.

Then we identify the unknowns. We need to solve for the mass of the ice, m . We also need to solve for the net heat transferred to melt the ice, Q . The rate of heat transfer by conduction is given by

Equation:

$$P = \frac{dQ}{dT} = \frac{kA(T_h - T_c)}{d}.$$

The heat used to melt the ice is $Q = mL_f$. We insert the known values:

Equation:

$$P = \frac{(0.010 \text{ W/m} \cdot ^\circ\text{C}) (0.950 \text{ m}^2) (35.0 ^\circ\text{C} - 0 ^\circ\text{C})}{0.0250 \text{ m}} = 13.3 \text{ W}.$$

Multiplying the rate of heat transfer by the time (1 day = 86,400 s), we obtain

Equation:

$$Q = Pt = (13.3 \text{ W}) (86,400 \text{ s}) = 1.15 \times 10^6 \text{ J}.$$

We set this equal to the heat transferred to melt the ice, $Q = mL_f$, and solve for the mass m :

Equation:

$$m = \frac{Q}{L_f} = \frac{1.15 \times 10^6 \text{ J}}{334 \times 10^3 \text{ J/kg}} = 3.44 \text{ kg}.$$

Significance

The result of 3.44 kg, or about 7.6 lb, seems about right, based on experience. You might expect to use about a 4 kg (7–10 lb) bag of ice per day. A little extra ice is required if you add any warm food or beverages.

[\[link\]](#) shows that polystyrene foam is a very poor conductor and thus a good insulator. Other good insulators include fiberglass, wool, and goose-down feathers. Like polystyrene foam, these all contain many small pockets of air, taking advantage of air's poor thermal conductivity.

In developing insulation, the smaller the conductivity k and the larger the thickness d , the better. Thus, the ratio d/k , called the *R factor*, is large for a good insulator. The rate of conductive heat transfer is inversely proportional to R . R factors are most commonly quoted for household insulation, refrigerators, and the like. Unfortunately, in the United States, R is still in non-metric units of $\text{ft}^2 \cdot ^\circ\text{F} \cdot \text{h}/\text{Btu}$, although the unit usually goes unstated [1 British thermal unit (Btu) is the amount of energy needed to change the temperature of 1.0 lb of water by $1.0 ^\circ\text{F}$, which is 1055.1 J]. A couple of representative values are an R factor of 11 for 3.5-inch-thick fiberglass batts (pieces) of insulation and an R factor of 19 for 6.5-inch-thick fiberglass batts ([\[link\]](#)). In the US, walls are usually insulated with 3.5-inch batts, whereas ceilings are usually insulated with 6.5-inch batts. In cold climates, thicker batts may be used.



The fiberglass batt is used for insulation of walls and ceilings to prevent heat transfer between the inside of the building and the outside environment. (credit: Tracey Nicholls)

Note that in [\[link\]](#), most of the best thermal conductors—silver, copper, gold, and aluminum—are also the best electrical conductors, because they contain many free electrons that can transport thermal energy. (Diamond, an electrical insulator, conducts heat by atomic vibrations.) Cooking utensils are typically made from good conductors, but the handles of those used on the stove are made from good insulators (bad conductors).

Example:
Two Conductors End to End

A steel rod and an aluminum rod, each of diameter 1.00 cm and length 25.0 cm, are welded end to end. One end of the steel rod is placed in a large tank of boiling water at 100°C , while the far end of the aluminum rod is placed in a large tank of water at 20°C . The rods are insulated so that no heat escapes from their surfaces. What is the temperature at the joint, and what is the rate of heat conduction through this composite rod?

Strategy

The heat that enters the steel rod from the boiling water has no place to go but through the steel rod, then through the aluminum rod, to the cold water. Therefore, we can equate the rate of conduction through the steel to the rate of conduction through the aluminum.

We repeat the calculation with a second method, in which we use the thermal resistance R of the rod, since it simply adds when two rods are joined end to end. (We will use a similar method in the chapter on direct-current circuits.)

Solution

1. Identify the knowns and convert them to SI units.

The length of each rod is $L_{\text{Al}} = L_{\text{steel}} = 0.25\text{ m}$, the cross-sectional area of each rod is $A_{\text{Al}} = A_{\text{steel}} = 7.85 \times 10^{-5}\text{ m}^2$, the thermal conductivity of aluminum is $k_{\text{Al}} = 220\text{ W/m}\cdot^\circ\text{C}$, the thermal conductivity of steel is $k_{\text{steel}} = 80\text{ W/m}\cdot^\circ\text{C}$, the temperature at the hot end is $T = 100^\circ\text{C}$, and the temperature at the cold end is $T = 20^\circ\text{C}$.

2. Calculate the heat-conduction rate through the steel rod and the heat-conduction rate through the aluminum rod in terms of the unknown temperature T at the joint:

Equation:

$$\begin{aligned} P_{\text{steel}} &= \frac{k_{\text{steel}} A_{\text{steel}} \Delta T_{\text{steel}}}{L_{\text{steel}}} \\ &= \frac{(80\text{ W/m}\cdot^\circ\text{C})(7.85 \times 10^{-5}\text{ m}^2)(100^\circ\text{C} - T)}{0.25\text{ m}} \\ &= (0.0251\text{ W}/^\circ\text{C})(100^\circ\text{C} - T); \end{aligned}$$

Equation:

$$\begin{aligned} P_{\text{Al}} &= \frac{k_{\text{Al}} A_{\text{Al}} \Delta T_{\text{Al}}}{L_{\text{Al}}} \\ &= \frac{(220\text{ W/m}\cdot^\circ\text{C})(7.85 \times 10^{-5}\text{ m}^2)(T - 20^\circ\text{C})}{0.25\text{ m}} \\ &= (0.0691\text{ W}/^\circ\text{C})(T - 20^\circ\text{C}). \end{aligned}$$

3. Set the two rates equal and solve for the unknown temperature:

Equation:

$$(0.0691 \text{ W/}^\circ\text{C}) (T - 20^\circ\text{C}) = (0.0251 \text{ W/}^\circ\text{C}) (100^\circ\text{C} - T)$$

$$T = 41.3^\circ\text{C}.$$

4. Calculate either rate:

Equation:

$$P_{\text{steel}} = (0.0251 \text{ W/}^\circ\text{C}) (100^\circ\text{C} - 41.3^\circ\text{C}) = 1.47 \text{ W}.$$

5. If desired, check your answer by calculating the other rate.

Solution

- Recall that $R = L/k$. Now $P = A\Delta T/R$, or $\Delta T = PR/A$.
- We know that $\Delta T_{\text{steel}} + \Delta T_{\text{Al}} = 100^\circ\text{C} - 20^\circ\text{C} = 80^\circ\text{C}$. We also know that $P_{\text{steel}} = P_{\text{Al}}$, and we denote that rate of heat flow by P . Combine the equations:

Equation:

$$\frac{PR_{\text{steel}}}{A} + \frac{PR_{\text{Al}}}{A} = 80^\circ\text{C}.$$

Thus, we can simply add R factors. Now, $P = \frac{80^\circ\text{C}}{A(R_{\text{steel}} + R_{\text{Al}})}.$

- Find the R_s from the known quantities:

Equation:

$$R_{\text{steel}} = 3.13 \times 10^{-3} \text{ m}^2 \cdot ^\circ\text{C/W}$$

and

Equation:

$$R_{\text{Al}} = 1.14 \times 10^{-3} \text{ m}^2 \cdot ^\circ\text{C/W}.$$

- Substitute these values in to find $P = 1.47 \text{ W}$ as before.
- Determine ΔT for the aluminum rod (or for the steel rod) and use it to find T at the joint.

Equation:

$$\Delta T_{\text{Al}} = \frac{PR_{\text{Al}}}{A} = \frac{(1.47 \text{ W}) (1.14 \times 10^{-3} \text{ m}^2 \cdot ^\circ\text{C/W})}{7.85 \times 10^{-5} \text{ m}^2} = 21.3^\circ\text{C},$$

so $T = 20^\circ\text{C} + 21.3^\circ\text{C} = 41.3^\circ\text{C}$, as in Solution 1.

- If desired, check by determining ΔT for the other rod.

Significance

In practice, adding R values is common, as in calculating the R value of an insulated wall. In the analogous situation in electronics, the resistance corresponds to AR in this problem and is additive even when the areas are unequal, as is common in electronics. Our equation for heat conduction can be used only when the areas are equal; otherwise, we would have a problem in three-dimensional heat flow, which is beyond our scope.

Note:

Exercise:

Problem:

Check Your Understanding How does the rate of heat transfer by conduction change when all spatial dimensions are doubled?

Solution:

Because area is the product of two spatial dimensions, it increases by a factor of four when each dimension is doubled ($A_{\text{final}} = (2d)^2 = 4d^2 = 4A_{\text{initial}}$). The distance, however, simply doubles. Because the temperature difference and the coefficient of thermal conductivity are independent of the spatial dimensions, the rate of heat transfer by conduction increases by a factor of four divided by two, or two:

$$P_{\text{final}} = \frac{kA_{\text{final}}(T_h - T_c)}{d_{\text{final}}} = \frac{k(4A_{\text{final}})(T_h - T_c)}{2d_{\text{initial}}} = 2 \frac{kA_{\text{final}}(T_h - T_c)}{d_{\text{initial}}} = 2P_{\text{initial}}.$$

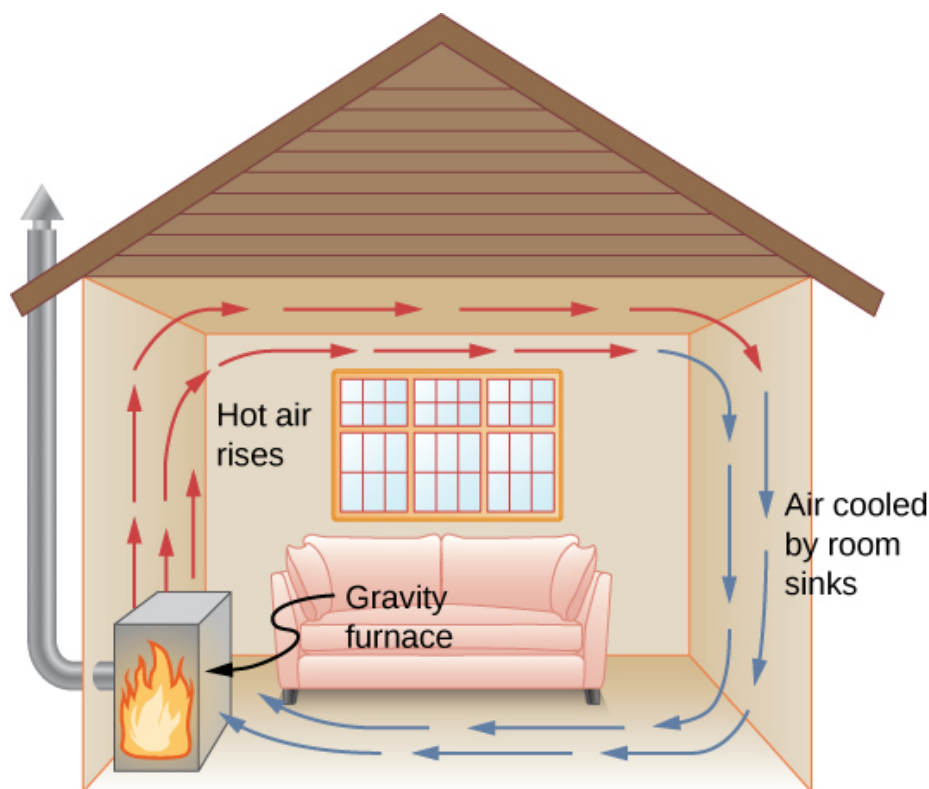
Conduction is caused by the random motion of atoms and molecules. As such, it is an ineffective mechanism for heat transport over macroscopic distances and short times. For example, the temperature on Earth would be unbearably cold during the night and extremely hot during the day if heat transport in the atmosphere were only through conduction. Also, car engines would overheat unless there was a more efficient way to remove excess heat from the pistons. The next module discusses the important heat-transfer mechanism in such situations.

Convection

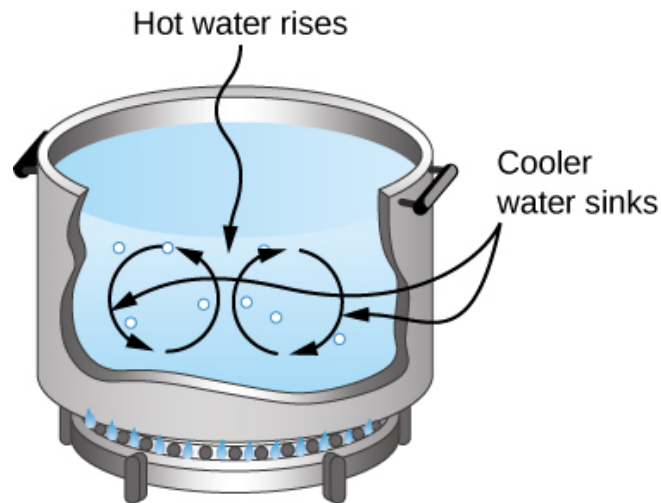
In convection, thermal energy is carried by the large-scale flow of matter. It can be divided into two types. In *forced convection*, the flow is driven by fans, pumps, and the like. A simple example is a fan that blows air past you in hot surroundings and cools

you by replacing the air heated by your body with cooler air. A more complicated example is the cooling system of a typical car, in which a pump moves coolant through the radiator and engine to cool the engine and a fan blows air to cool the radiator.

In *free or natural convection*, the flow is driven by buoyant forces: hot fluid rises and cold fluid sinks because density decreases as temperature increases. The house in [\[link\]](#) is kept warm by natural convection, as is the pot of water on the stove in [\[link\]](#). Ocean currents and large-scale atmospheric circulation, which result from the buoyancy of warm air and water, transfer hot air from the tropics toward the poles and cold air from the poles toward the tropics. (Earth's rotation interacts with those flows, causing the observed eastward flow of air in the temperate zones.)



Air heated by a so-called gravity furnace expands and rises, forming a convective loop that transfers energy to other parts of the room. As the air is cooled at the ceiling and outside walls, it contracts, eventually becoming denser than room air and sinking to the floor. A properly designed heating system using natural convection, like this one, can heat a home quite efficiently.



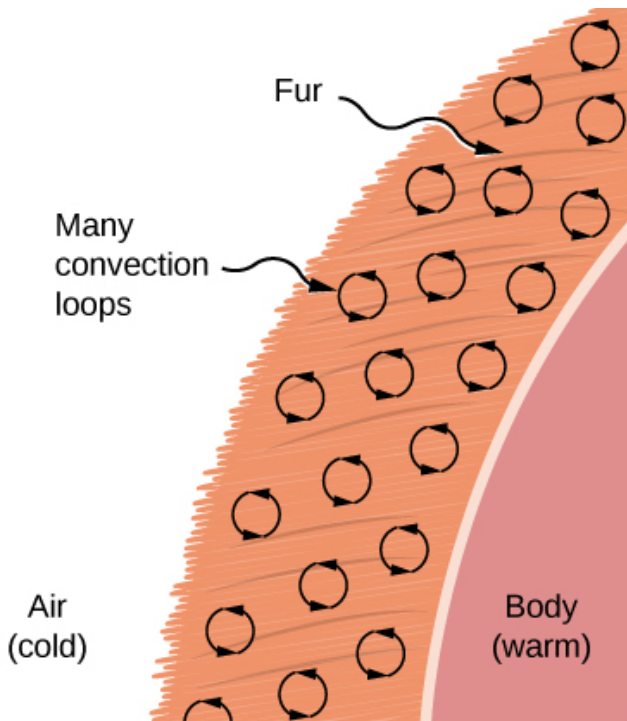
Natural convection plays an important role in heat transfer inside this pot of water. Once conducted to the inside, heat transfer to other parts of the pot is mostly by convection. The hotter water expands, decreases in density, and rises to transfer heat to other regions of the water, while colder water sinks to the bottom. This process keeps repeating.

Note:

Natural convection like that of [link](#) and [link](#), but acting on rock in Earth's mantle, drives [plate tectonics](#) that are the motions that have shaped Earth's surface.

Convection is usually more complicated than conduction. Beyond noting that the convection rate is often approximately proportional to the temperature difference, we will not do any quantitative work comparable to the formula for conduction. However, we can describe convection qualitatively and relate convection rates to heat and time. However, air is a poor conductor. Therefore, convection dominates heat transfer by air, and the amount of available space for airflow determines whether air transfers heat rapidly or slowly. There is little heat transfer in a space filled with air with a small amount of other material that prevents flow. The space between the inside and outside walls of a typical American house, for example, is about 9 cm (3.5 in.)—large enough for convection to work effectively. The addition of wall insulation prevents airflow, so

heat loss (or gain) is decreased. On the other hand, the gap between the two panes of a double-paned window is about 1 cm, which largely prevents convection and takes advantage of air's low conductivity reduce heat loss. Fur, cloth, and fiberglass also take advantage of the low conductivity of air by trapping it in spaces too small to support convection ([link](#)).



Fur is filled with air, breaking it up into many small pockets. Convection is very slow here, because the loops are so small. The low conductivity of air makes fur a very good lightweight insulator.

Some interesting phenomena happen when convection is accompanied by a phase change. The combination allows us to cool off by sweating even if the temperature of the surrounding air exceeds body temperature. Heat from the skin is required for sweat to evaporate from the skin, but without air flow, the air becomes saturated and evaporation stops. Air flow caused by convection replaces the saturated air by dry air and evaporation continues.

Example:**Calculating the Flow of Mass during Convection**

The average person produces heat at the rate of about 120 W when at rest. At what rate must water evaporate from the body to get rid of all this energy? (For simplicity, we assume this evaporation occurs when a person is sitting in the shade and surrounding temperatures are the same as skin temperature, eliminating heat transfer by other methods.)

Strategy

Energy is needed for this phase change ($Q = mL_v$). Thus, the energy loss per unit time is

Equation:

$$\frac{Q}{t} = \frac{mL_v}{t} = 120 \text{ W} = 120 \text{ J/s}.$$

We divide both sides of the equation by L_v to find that the mass evaporated per unit time is

Equation:

$$\frac{m}{t} = \frac{120 \text{ J/s}}{L_v}.$$

Solution

Insert the value of the latent heat from [\[link\]](#), $L_v = 2430 \text{ kJ/kg} = 2430 \text{ J/g}$. This yields

Equation:

$$\frac{m}{t} = \frac{120 \text{ J/s}}{2430 \text{ J/g}} = 0.0494 \text{ g/s} = 2.96 \text{ g/min}.$$

Significance

Evaporating about 3 g/min seems reasonable. This would be about 180 g (about 7 oz.) per hour. If the air is very dry, the sweat may evaporate without even being noticed. A significant amount of evaporation also takes place in the lungs and breathing passages.

Another important example of the combination of phase change and convection occurs when water evaporates from the oceans. Heat is removed from the ocean when water evaporates. If the water vapor condenses in liquid droplets as clouds form, possibly far from the ocean, heat is released in the atmosphere. Thus, there is an overall transfer of heat from the ocean to the atmosphere. This process is the driving power behind thunderheads, those great cumulus clouds that rise as much as 20.0 km into the stratosphere ([\[link\]](#)). Water vapor carried in by convection condenses, releasing

tremendous amounts of energy. This energy causes the air to expand and rise to colder altitudes. More condensation occurs in these regions, which in turn drives the cloud even higher. This mechanism is an example of positive feedback, since the process reinforces and accelerates itself. It sometimes produces violent storms, with lightning and hail. The same mechanism drives hurricanes.

Note:

This [time-lapse video](#) shows convection currents in a thunderstorm, including “rolling” motion similar to that of boiling water.



Cumulus clouds are caused by water vapor that rises because of convection. The rise of clouds is driven by a positive feedback mechanism. (credit: “Amada44”/Wikimedia Commons)

Note:

Exercise:

Problem:

Check Your Understanding Explain why using a fan in the summer feels refreshing.

Solution:

Using a fan increases the flow of air: Warm air near your body is replaced by cooler air from elsewhere. Convection increases the rate of heat transfer so that moving air “feels” cooler than still air.

Radiation

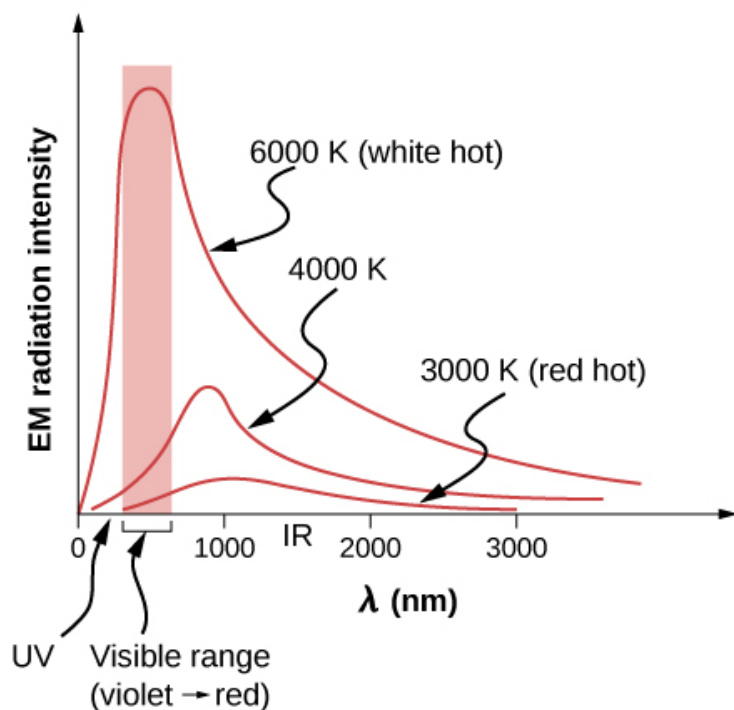
You can feel the heat transfer from the Sun. The space between Earth and the Sun is largely empty, so the Sun warms us without any possibility of heat transfer by convection or conduction. Similarly, you can sometimes tell that the oven is hot without touching its door or looking inside—it may just warm you as you walk by. In these examples, heat is transferred by radiation ([link](#)). That is, the hot body emits electromagnetic waves that are absorbed by the skin. No medium is required for electromagnetic waves to propagate. Different names are used for electromagnetic waves of different wavelengths: radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays, and gamma rays.



Most of the heat transfer from this fire to the observers

occurs through infrared radiation. The visible light, although dramatic, transfers relatively little thermal energy. Convection transfers energy away from the observers as hot air rises, while conduction is negligibly slow here. Skin is very sensitive to infrared radiation, so you can sense the presence of a fire without looking at it directly. (credit: Daniel O'Neil)

The energy of electromagnetic radiation varies over a wide range, depending on the wavelength: A shorter wavelength (or higher frequency) corresponds to a higher energy. Because more heat is radiated at higher temperatures, higher temperatures produce more intensity at every wavelength but especially at shorter wavelengths. In visible light, wavelength determines color—red has the longest wavelength and violet the shortest—so a temperature change is accompanied by a color change. For example, an electric heating element on a stove glows from red to orange, while the higher-temperature steel in a blast furnace glows from yellow to white. Infrared radiation is the predominant form radiated by objects cooler than the electric element and the steel. The radiated energy as a function of wavelength depends on its intensity, which is represented in [\[link\]](#) by the height of the distribution. ([Electromagnetic Waves](#) explains more about the electromagnetic spectrum, and [Photons and Matter Waves](#) discusses why the decrease in wavelength corresponds to an increase in energy.)



(a)

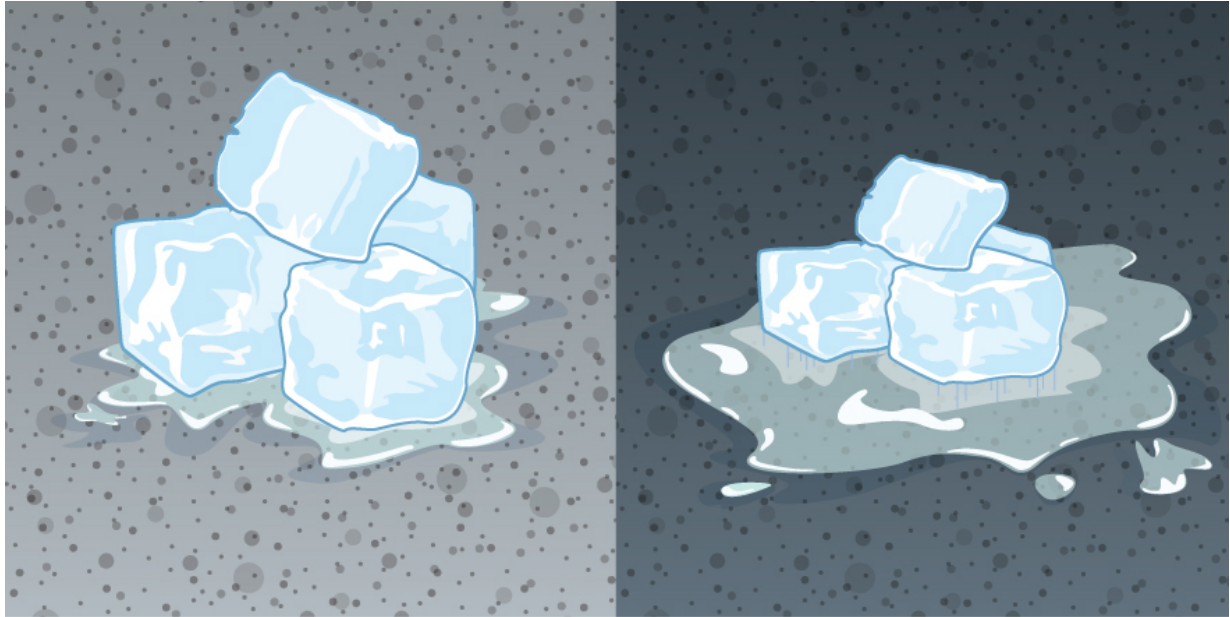


(b)

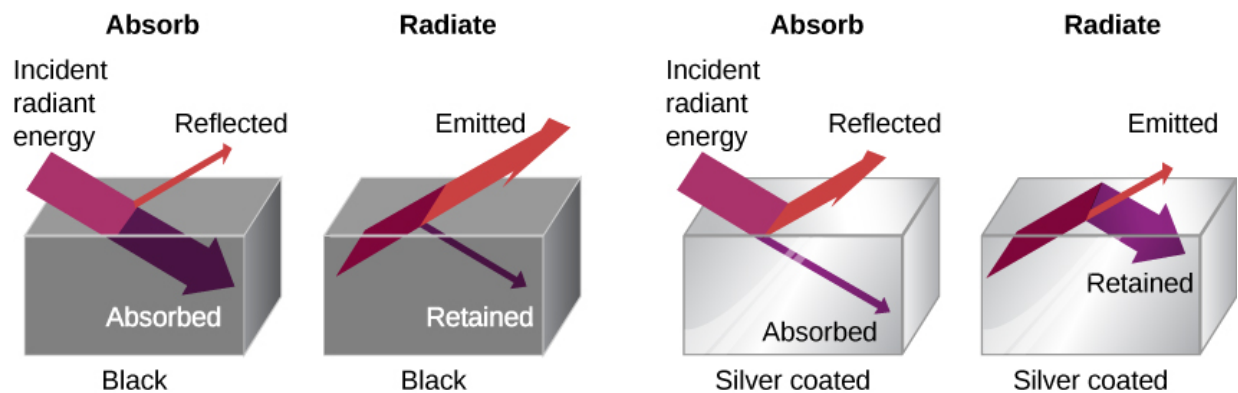
(a) A graph of the spectrum of electromagnetic waves emitted from an ideal radiator at three different temperatures. The intensity or rate of radiation emission increases dramatically with temperature, and the spectrum shifts down in wavelength toward the visible and ultraviolet parts of the spectrum. The shaded portion denotes the visible part of the spectrum. It is apparent that the shift toward the ultraviolet with temperature makes the visible appearance shift from red to white to blue as temperature increases. (b) Note the variations in color corresponding to variations in flame temperature.

The rate of heat transfer by radiation also depends on the object's color. Black is the most effective, and white is the least effective. On a clear summer day, black asphalt in a parking lot is hotter than adjacent gray sidewalk, because black absorbs better than gray ([link](#)). The reverse is also true—black radiates better than gray. Thus, on a clear summer night, the asphalt is colder than the gray sidewalk, because black radiates the energy more rapidly than gray. A perfectly black object would be an *ideal radiator* and an *ideal absorber*, as it would capture all the radiation that falls on it. In contrast, a perfectly white object or a perfect mirror would reflect all radiation, and a perfectly transparent object would transmit it all ([link](#)). Such objects would not emit any radiation. Mathematically, the color is represented by the **emissivity** e . A “blackbody” radiator would have an $e = 1$, whereas a perfect reflector or transmitter would have

$e = 0$. For real examples, tungsten light bulb filaments have an e of about 0.5, and carbon black (a material used in printer toner) has an emissivity of about 0.95.



The darker pavement is hotter than the lighter pavement (much more of the ice on the right has melted), although both have been in the sunlight for the same time.
The thermal conductivities of the pavements are the same.



A black object is a good absorber and a good radiator, whereas a white, clear, or silver object is a poor absorber and a poor radiator.

To see that, consider a silver object and a black object that can exchange heat by radiation and are in thermal equilibrium. We know from experience that they will stay in equilibrium (the result of a principle that will be discussed at length in [Second Law of Thermodynamics](#)). For the black object's temperature to stay constant, it must emit as much radiation as it absorbs, so it must be as good at radiating as absorbing. Similar considerations show that the silver object must radiate as little as it absorbs. Thus, one property, emissivity, controls both radiation and absorption.

Finally, the radiated heat is proportional to the object's surface area, since every part of the surface radiates. If you knock apart the coals of a fire, the radiation increases noticeably due to an increase in radiating surface area.

The rate of heat transfer by emitted radiation is described by the **Stefan-Boltzmann law of radiation**:

Equation:

$$P = \sigma A e T^4,$$

where $\sigma = 5.67 \times 10^{-8} \text{ J/s} \cdot \text{m}^2 \cdot \text{K}^4$ is the Stefan-Boltzmann constant, a combination of fundamental constants of nature; A is the surface area of the object; and T is its temperature in kelvins.

The proportionality to the *fourth power* of the absolute temperature is a remarkably strong temperature dependence. It allows the detection of even small temperature variations. Images called *thermographs* can be used medically to detect regions of abnormally high temperature in the body, perhaps indicative of disease. Similar techniques can be used to detect heat leaks in homes ([\[link\]](#)), optimize performance of blast furnaces, improve comfort levels in work environments, and even remotely map Earth's temperature profile.



A thermograph of part of a building shows temperature variations, indicating where heat transfer to the outside is most severe. Windows are a major region of heat transfer to the outside of homes. (credit: US Army)

The Stefan-Boltzmann equation needs only slight refinement to deal with a simple case of an object's absorption of radiation from its surroundings. Assuming that an object with a temperature T_1 is surrounded by an environment with uniform temperature T_2 , the **net rate of heat transfer by radiation** is

Note:

Equation:

$$P_{\text{net}} = \sigma e A (T_2^4 - T_1^4),$$

where e is the emissivity of the object alone. In other words, it does not matter whether the surroundings are white, gray, or black: The balance of radiation into and out of the object depends on how well it emits and absorbs radiation. When $T_2 > T_1$, the quantity P_{net} is positive, that is, the net heat transfer is from hot to cold.

Before doing an example, we have a complication to discuss: different emissivities at different wavelengths. If the fraction of incident radiation an object reflects is the same at all visible wavelengths, the object is gray; if the fraction depends on the wavelength, the object has some other color. For instance, a red or reddish object reflects red light more strongly than other visible wavelengths. Because it absorbs less red, it radiates less red when hot. Differential reflection and absorption of wavelengths outside the visible range have no effect on what we see, but they may have physically important effects. Skin is a very good absorber and emitter of infrared radiation, having an emissivity of 0.97 in the infrared spectrum. Thus, in spite of the obvious variations in skin color, we are all nearly black in the infrared. This high infrared emissivity is why we can so easily feel radiation on our skin. It is also the basis for the effectiveness of night-vision scopes used by law enforcement and the military to detect human beings.

Example:**Calculating the Net Heat Transfer of a Person**

What is the rate of heat transfer by radiation of an unclothed person standing in a dark room whose ambient temperature is 22.0°C ? The person has a normal skin temperature of 33.0°C and a surface area of 1.50 m^2 . The emissivity of skin is 0.97 in the infrared, the part of the spectrum where the radiation takes place.

Strategy

We can solve this by using the equation for the rate of radiative heat transfer.

Solution

Insert the temperature values $T_2 = 295\text{ K}$ and $T_1 = 306\text{ K}$, so that

Equation:

$$\begin{aligned}\frac{Q}{t} &= \sigma e A (T_2^4 - T_1^4) \\ &= (5.67 \times 10^{-8} \text{ J/s} \cdot \text{m}^2 \cdot \text{K}^4) (0.97) (1.50 \text{ m}^2) [(295 \text{ K})^4 - (306 \text{ K})^4] \\ &= -99 \text{ J/s} = -99 \text{ W}.\end{aligned}$$

Significance

This value is a significant rate of heat transfer to the environment (note the minus sign), considering that a person at rest may produce energy at the rate of 125 W and that conduction and convection are also transferring energy to the environment. Indeed, we would probably expect this person to feel cold. Clothing significantly reduces heat transfer to the environment by all mechanisms, because clothing slows down both

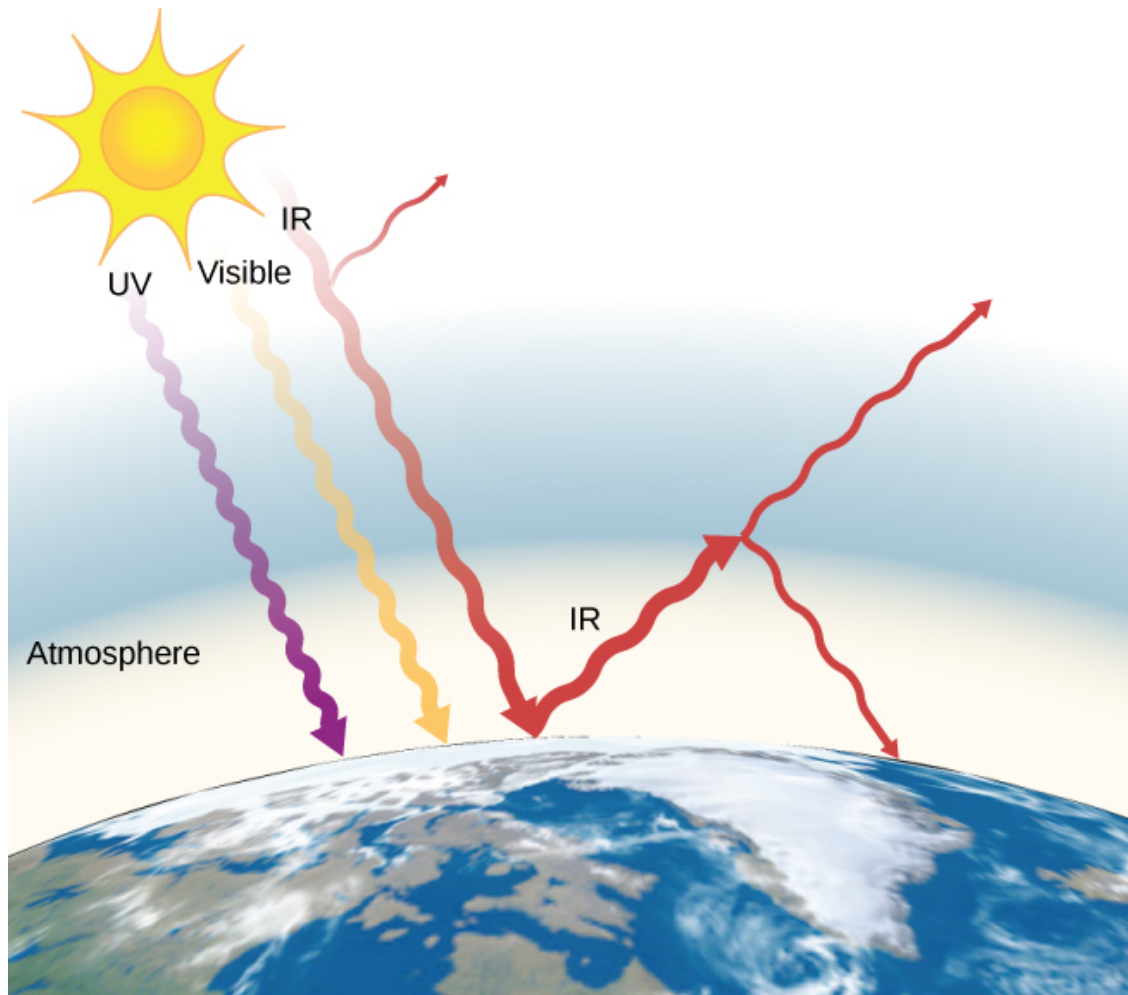
conduction and convection, and has a lower emissivity (especially if it is light-colored) than skin.

The average temperature of Earth is the subject of much current discussion. Earth is in radiative contact with both the Sun and dark space, so we cannot use the equation for an environment at a uniform temperature. Earth receives almost all its energy from radiation of the Sun and reflects some of it back into outer space. Conversely, dark space is very cold, about 3 K, so that Earth radiates energy into the dark sky. The rate of heat transfer from soil and grasses can be so rapid that frost may occur on clear summer evenings, even in warm latitudes.

The average temperature of Earth is determined by its energy balance. To a first approximation, it is the temperature at which Earth radiates heat to space as fast as it receives energy from the Sun.

An important parameter in calculating the temperature of Earth is its emissivity (e). On average, it is about 0.65, but calculation of this value is complicated by the great day-to-day variation in the highly reflective cloud coverage. Because clouds have lower emissivity than either oceans or land masses, they reflect some of the radiation back to the surface, greatly reducing heat transfer into dark space, just as they greatly reduce heat transfer into the atmosphere during the day. There is negative feedback (in which a change produces an effect that opposes that change) between clouds and heat transfer; higher temperatures evaporate more water to form more clouds, which reflect more radiation back into space, reducing the temperature.

The often-mentioned **greenhouse effect** is directly related to the variation of Earth's emissivity with wavelength ([\[link\]](#)). The greenhouse effect is a natural phenomenon responsible for providing temperatures suitable for life on Earth and for making Venus unsuitable for human life. Most of the infrared radiation emitted from Earth is absorbed by carbon dioxide (CO₂) and water (H₂O) in the atmosphere and then re-radiated into outer space or back to Earth. Re-radiation back to Earth maintains its surface temperature about 40 °C higher than it would be if there were no atmosphere. (The glass walls and roof of a greenhouse increase the temperature inside by blocking convective heat losses, not radiative losses.)



The greenhouse effect is the name given to the increase of Earth's temperature due to absorption of radiation in the atmosphere. The atmosphere is transparent to incoming visible radiation and most of the Sun's infrared. The Earth absorbs that energy and re-emits it. Since Earth's temperature is much lower than the Sun's, it re-emits the energy at much longer wavelengths, in the infrared. The atmosphere absorbs much of that infrared radiation and radiates about half of the energy back down, keeping Earth warmer than it would otherwise be. The amount of trapping depends on concentrations of trace gases such as carbon dioxide, and an increase in the concentration of these gases increases Earth's surface temperature.

The greenhouse effect is central to the discussion of global warming due to emission of carbon dioxide and methane (and other greenhouse gases) into Earth's atmosphere from industry, transportation, and farming. Changes in global climate could lead to more

intense storms, precipitation changes (affecting agriculture), reduction in rain forest biodiversity, and rising sea levels.

Note:

You can explore [a simulation of the greenhouse effect](#) that takes the point of view that the atmosphere scatters (redirects) infrared radiation rather than absorbing it and reradiating it. You may want to run the simulation first with no greenhouse gases in the atmosphere and then look at how adding greenhouse gases affects the infrared radiation from the Earth and the Earth's temperature.

Note:

Problem-Solving Strategy: Effects of Heat Transfer

1. Examine the situation to determine what type of heat transfer is involved.
2. Identify the type(s) of heat transfer—conduction, convection, or radiation.
3. Identify exactly what needs to be determined in the problem (identify the unknowns). A written list is useful.
4. Make a list of what is given or what can be inferred from the problem as stated (identify the knowns).
5. Solve the appropriate equation for the quantity to be determined (the unknown).
6. For conduction, use the equation $P = \frac{kA\Delta T}{d}$. [\[link\]](#) lists thermal conductivities. For convection, determine the amount of matter moved and the equation $Q = mc\Delta T$, along with $Q = mL_f$ or $Q = mL_v$ if a substance changes phase. For radiation, the equation $P_{\text{net}} = \sigma eA (T_2^4 - T_1^4)$ gives the net heat transfer rate.
7. Substitute the knowns along with their units into the appropriate equation and obtain numerical solutions complete with units.
8. Check the answer to see if it is reasonable. Does it make sense?

Note:

Exercise:

Problem:

Check Your Understanding How much greater is the rate of heat radiation when a body is at the temperature 40°C than when it is at the temperature 20°C ?

Solution:

The radiated heat is proportional to the fourth power of the *absolute temperature*. Because $T_1 = 293\text{ K}$ and $T_2 = 313\text{ K}$, the rate of heat transfer increases by about 30% of the original rate.

Summary

- Heat is transferred by three different methods: conduction, convection, and radiation.
- Heat conduction is the transfer of heat between two objects in direct contact with each other.
- The rate of heat transfer P (energy per unit time) is proportional to the temperature difference $T_h - T_c$ and the contact area A and inversely proportional to the distance d between the objects.
- Convection is heat transfer by the macroscopic movement of mass. Convection can be natural or forced, and generally transfers thermal energy faster than conduction. Convection that occurs along with a phase change can transfer energy from cold regions to warm ones.
- Radiation is heat transfer through the emission or absorption of electromagnetic waves.
- The rate of radiative heat transfer is proportional to the emissivity e . For a perfect blackbody, $e = 1$, whereas a perfectly white, clear, or reflective body has $e = 0$, with real objects having values of e between 1 and 0.
- The rate of heat transfer depends on the surface area and the fourth power of the absolute temperature:

Equation:

$$P = \sigma e A T^4,$$

where $\sigma = 5.67 \times 10^{-8}\text{ J/s} \cdot \text{m}^2 \cdot \text{K}^4$ is the Stefan-Boltzmann constant and e is the emissivity of the body. The net rate of heat transfer from an object by radiation is

Equation:

$$\frac{Q_{\text{net}}}{t} = \sigma e A (T_2^4 - T_1^4),$$

where T_1 is the temperature of the object surrounded by an environment with

uniform temperature T_2 and e is the emissivity of the object.

Key Equations

Linear thermal expansion	$\Delta L = \alpha L \Delta T$
Thermal expansion in two dimensions	$\Delta A = 2\alpha A \Delta T$
Thermal expansion in three dimensions	$\Delta V = \beta V \Delta T$
Heat transfer	$Q = mc\Delta T$
Transfer of heat in a calorimeter	$Q_{\text{cold}} + Q_{\text{hot}} = 0$
Heat due to phase change (melting and freezing)	$Q = mL_f$
Heat due to phase change (evaporation and condensation)	$Q = mL_v$
Rate of conductive heat transfer	$P = \frac{kA(T_h - T_c)}{d}$
Net rate of heat transfer by radiation	$P_{\text{net}} = \sigma e A (T_2^4 - T_1^4)$

Conceptual Questions

Exercise:

Problem:

What are the main methods of heat transfer from the hot core of Earth to its surface? From Earth's surface to outer space?

Exercise:

Problem:

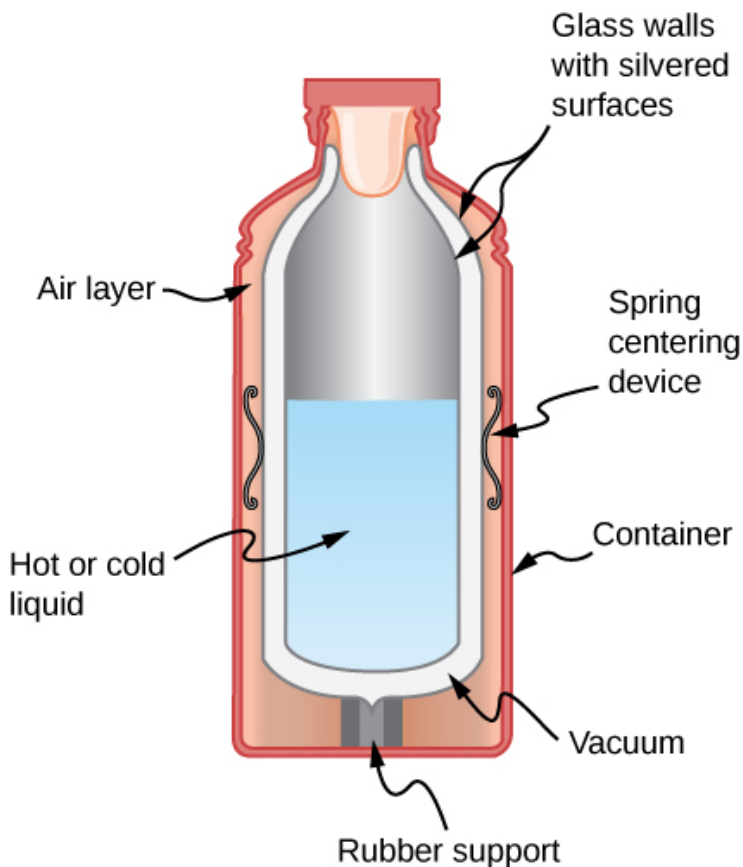
When our bodies get too warm, they respond by sweating and increasing blood circulation to the surface to transfer thermal energy away from the core. What effect will those processes have on a person in a 40.0°C hot tub?

Solution:

Increasing circulation to the surface will warm the person, as the temperature of the water is warmer than human body temperature. Sweating will cause no evaporative cooling under water or in the humid air immediately above the tub.

Exercise:**Problem:**

Shown below is a cut-away drawing of a thermos bottle (also known as a Dewar flask), which is a device designed specifically to slow down all forms of heat transfer. Explain the functions of the various parts, such as the vacuum, the silvering of the walls, the thin-walled long glass neck, the rubber support, the air layer, and the stopper.



Exercise:**Problem:**

Some electric stoves have a flat ceramic surface with heating elements hidden beneath. A pot placed over a heating element will be heated, while the surface only a few centimeters away is safe to touch. Why is ceramic, with a conductivity less than that of a metal but greater than that of a good insulator, an ideal choice for the stove top?

Solution:

It spread the heat over the area above the heating elements, evening the temperature there, but does not spread the heat much beyond the heating elements.

Exercise:**Problem:**

Loose-fitting white clothing covering most of the body, shown below, is ideal for desert dwellers, both in the hot Sun and during cold evenings. Explain how such clothing is advantageous during both day and night.



Exercise:

Problem:

One way to make a fireplace more energy-efficient is to have room air circulate around the outside of the fire box and back into the room. Detail the methods of heat transfer involved.

Solution:

Heat is conducted from the fire through the fire box to the circulating air and then convected by the air into the room (forced convection).

Exercise:

Problem:

On cold, clear nights horses will sleep under the cover of large trees. How does this help them keep warm?

Exercise:**Problem:**

When watching a circus during the day in a large, dark-colored tent, you sense significant heat transfer from the tent. Explain why this occurs.

Solution:

The tent is heated by the Sun and transfers heat to you by all three processes, especially radiation.

Exercise:**Problem:**

Satellites designed to observe the radiation from cold (3 K) dark space have sensors that are shaded from the Sun, Earth, and the Moon and are cooled to very low temperatures. Why must the sensors be at low temperature?

Exercise:**Problem:**

Why are thermometers that are used in weather stations shielded from the sunshine? What does a thermometer measure if it is shielded from the sunshine? What does it measure if it is not?

Solution:

If shielded, it measures the air temperature. If not, it measures the combined effect of air temperature and net radiative heat gain from the Sun.

Exercise:**Problem:**

Putting a lid on a boiling pot greatly reduces the heat transfer necessary to keep it boiling. Explain why.

Exercise:

Problem:

Your house will be empty for a while in cold weather, and you want to save energy and money. Should you turn the thermostat down to the lowest level that will protect the house from damage such as freezing pipes, or leave it at the normal temperature? (If you don't like coming back to a cold house, imagine that a timer controls the heating system so the house will be warm when you get back.) Explain your answer.

Solution:

Turn the thermostat down. To have the house at the normal temperature, the heating system must replace all the heat that was lost. For all three mechanisms of heat transfer, the greater the temperature difference between inside and outside, the more heat is lost and must be replaced. So the house should be at the lowest temperature that does not allow freezing damage.

Exercise:**Problem:**

You pour coffee into an unlidged cup, intending to drink it 5 minutes later. You can add cream when you pour the cup or right before you drink it. (The cream is at the same temperature either way. Assume that the cream and coffee come into thermal equilibrium with each other very quickly.) Which way will give you hotter coffee? What feature of this question is different from the previous one?

Exercise:**Problem:**

Broiling is a method of cooking by radiation, which produces somewhat different results from cooking by conduction or convection. A gas flame or electric heating element produces a very high temperature close to the food and *above* it. Why is radiation the dominant heat-transfer method in this situation?

Solution:

Air is a good insulator, so there is little conduction, and the heated air rises, so there is little convection downward.

Exercise:**Problem:**

On a cold winter morning, why does the metal of a bike feel colder than the wood of a porch?

Problems

Exercise:

Problem:

(a) Calculate the rate of heat conduction through house walls that are 13.0 cm thick and have an average thermal conductivity twice that of glass wool. Assume there are no windows or doors. The walls' surface area is 120 m^2 and their inside surface is at 18.0°C , while their outside surface is at 5.00°C . (b) How many 1-kW room heaters would be needed to balance the heat transfer due to conduction?

Solution:

a. $1.01 \times 10^3 \text{ W}$; b. One 1-kilowatt room heater is needed.

Exercise:

Problem:

The rate of heat conduction out of a window on a winter day is rapid enough to chill the air next to it. To see just how rapidly the windows transfer heat by conduction, calculate the rate of conduction in watts through a 3.00-m^2 window that is 0.634 cm thick ($1/4$ in.) if the temperatures of the inner and outer surfaces are 5.00°C and -10.0°C , respectively. (This rapid rate will not be maintained—the inner surface will cool, even to the point of frost formation.)

Exercise:

Problem:

Calculate the rate of heat conduction out of the human body, assuming that the core internal temperature is 37.0°C , the skin temperature is 34.0°C , the thickness of the fatty tissues between the core and the skin averages 1.00 cm, and the surface area is 1.40 m^2 .

Solution:

84.0 W

Exercise:

Problem:

Suppose you stand with one foot on ceramic flooring and one foot on a wool carpet, making contact over an area of 80.0 cm^2 with each foot. Both the ceramic and the carpet are 2.00 cm thick and are 10.0°C on their bottom sides. At what rate must heat transfer occur from each foot to keep the top of the ceramic and carpet at 33.0°C ?

Exercise:**Problem:**

A man consumes 3000 kcal of food in one day, converting most of it to thermal energy to maintain body temperature. If he loses half this energy by evaporating water (through breathing and sweating), how many kilograms of water evaporate?

Solution:

2.59 kg

Exercise:**Problem:**

A firewalker runs across a bed of hot coals without sustaining burns. Calculate the heat transferred by conduction into the sole of one foot of a firewalker given that the bottom of the foot is a 3.00-mm -thick callus with a conductivity at the low end of the range for wood and its density is 300 kg/m^3 . The area of contact is 25.0 cm^2 , the temperature of the coals is 700°C , and the time in contact is 1.00 s . Ignore the evaporative cooling of sweat.

Exercise:**Problem:**

(a) What is the rate of heat conduction through the 3.00-cm -thick fur of a large animal having a 1.40-m^2 surface area? Assume that the animal's skin temperature is 32.0°C , that the air temperature is -5.00°C , and that fur has the same thermal conductivity as air. (b) What food intake will the animal need in one day to replace this heat transfer?

Solution:

a. 39.7 W ; b. 820 kcal

Exercise:

Problem:

A walrus transfers energy by conduction through its blubber at the rate of 150 W when immersed in $-1.00\text{ }^{\circ}\text{C}$ water. The walrus's internal core temperature is $37.0\text{ }^{\circ}\text{C}$, and it has a surface area of 2.00 m^2 . What is the average thickness of its blubber, which has the conductivity of fatty tissues without blood?

Exercise:**Problem:**

Compare the rate of heat conduction through a 13.0-cm-thick wall that has an area of 10.0 m^2 and a thermal conductivity twice that of glass wool with the rate of heat conduction through a 0.750-cm-thick window that has an area of 2.00 m^2 , assuming the same temperature difference across each.

Solution:

$$\frac{Q}{t} = \frac{kA(T_2 - T_1)}{d}, \text{ so that}$$

$$\frac{(Q/t)_{\text{wall}}}{(Q/t)_{\text{window}}} = \frac{k_{\text{wall}}A_{\text{wall}}d_{\text{window}}}{k_{\text{window}}A_{\text{window}}d_{\text{wall}}} = \frac{(2 \times 0.042\text{ J/s}\cdot\text{m}\cdot^{\circ}\text{C})(10.0\text{ m}^2)(0.750 \times 10^{-2}\text{ m})}{(0.84\text{ J/s}\cdot\text{m}\cdot^{\circ}\text{C})(2.00\text{ m}^2)(13.0 \times 10^{-2}\text{ m})}$$

This gives 0.0288 wall: window, or 35:1 window: wall

Exercise:**Problem:**

Suppose a person is covered head to foot by wool clothing with average thickness of 2.00 cm and is transferring energy by conduction through the clothing at the rate of 50.0 W. What is the temperature difference across the clothing, given the surface area is 1.40 m^2 ?

Exercise:**Problem:**

Some stove tops are smooth ceramic for easy cleaning. If the ceramic is 0.600 cm thick and heat conduction occurs through the same area and at the same rate as computed in [\[link\]](#), what is the temperature difference across it? Ceramic has the same thermal conductivity as glass and brick.

Solution:

$$\frac{Q}{t} = \frac{kA(T_2 - T_1)}{d} = \frac{kA\Delta T}{d} \Rightarrow$$

$$\Delta T = \frac{d(Q/t)}{kA} = \frac{(6.00 \times 10^{-3}\text{ m})(2256\text{ W})}{(0.84\text{ J/s}\cdot\text{m}\cdot^{\circ}\text{C})(1.54 \times 10^{-2}\text{ m}^2)} = 1046\text{ }^{\circ}\text{C} = 1.05 \times 10^3\text{ K}$$

Exercise:**Problem:**

One easy way to reduce heating (and cooling) costs is to add extra insulation in the attic of a house. Suppose a single-story cubical house already had 15 cm of fiberglass insulation in the attic and in all the exterior surfaces. If you added an extra 8.0 cm of fiberglass to the attic, by what percentage would the heating cost of the house drop? Take the house to have dimensions 10 m by 15 m by 3.0 m. Ignore air infiltration and heat loss through windows and doors, and assume that the interior is uniformly at one temperature and the exterior is uniformly at another.

Exercise:**Problem:**

Many decisions are made on the basis of the payback period: the time it will take through savings to equal the capital cost of an investment. Acceptable payback times depend upon the business or philosophy one has. (For some industries, a payback period is as small as 2 years.) Suppose you wish to install the extra insulation in the preceding problem. If energy cost \$1.00 per million joules and the insulation was \$4.00 per square meter, then calculate the simple payback time. Take the average ΔT for the 120-day heating season to be 15.0 °C.

Solution:

We found in the preceding problem that $P = 126\Delta T \text{ W} \cdot ^\circ\text{C}$ as baseline energy use. So the total heat loss during this period is
 $Q = (126 \text{ J/s} \cdot ^\circ\text{C}) (15.0 ^\circ\text{C}) (120 \text{ days}) (86.4 \times 10^3 \text{ s/day}) = 1960 \times 10^6 \text{ J}$
. At the cost of \$1/MJ, the cost is \$1960. From an earlier problem, the savings is 12% or \$235/y. We need 150 m² of insulation in the attic. At \$4/m², this is a \$500 cost. So the payback period is $\$600 / (\$235/\text{y}) = 2.6 \text{ years}$ (excluding labor costs).

Additional Problems**Exercise:****Problem:**

In 1701, the Danish astronomer Ole Rømer proposed a temperature scale with two fixed points, freezing water at 7.5 degrees, and boiling water at 60.0 degrees. What is the boiling point of oxygen, 90.2 K, on the Rømer scale?

Exercise:

Problem:

What is the percent error of thinking the melting point of tungsten is 3695°C instead of the correct value of 3695 K ?

Solution:

$$7.39\%$$

Exercise:**Problem:**

An engineer wants to design a structure in which the difference in length between a steel beam and an aluminum beam remains at 0.500 m regardless of temperature, for ordinary temperatures. What must the lengths of the beams be?

Exercise:**Problem:**

How much stress is created in a steel beam if its temperature changes from -15°C to 40°C but it cannot expand? For steel, the Young's modulus $Y = 210 \times 10^9\text{ N/m}^2$ from [Stress, Strain, and Elastic Modulus](#). (Ignore the change in area resulting from the expansion.)

Solution:

$$\frac{F}{A} = (210 \times 10^9\text{ Pa}) (12 \times 10^{-6}/^{\circ}\text{C}) (40^{\circ}\text{C} - (-15^{\circ}\text{C})) = 1.4 \times 10^8\text{ N/m}^2$$

Exercise:**Problem:**

A brass rod ($Y = 90 \times 10^9\text{ N/m}^2$), with a diameter of 0.800 cm and a length of 1.20 m when the temperature is 25°C , is fixed at both ends. At what temperature is the force in it at $36,000\text{ N}$?

Exercise:

Problem:

A mercury thermometer still in use for meteorology has a bulb with a volume of 0.780 cm^3 and a tube for the mercury to expand into of inside diameter 0.130 mm . (a) Neglecting the thermal expansion of the glass, what is the spacing between marks 1°C apart? (b) If the thermometer is made of ordinary glass (not a good idea), what is the spacing?

Solution:

a. 1.06 cm ; b. 1.11 cm

Exercise:**Problem:**

Even when shut down after a period of normal use, a large commercial nuclear reactor transfers thermal energy at the rate of 150 MW by the radioactive decay of fission products. This heat transfer causes a rapid increase in temperature if the cooling system fails ($1 \text{ watt} = 1 \text{ joule/second}$ or $1 \text{ W} = 1 \text{ J/s}$ and $1 \text{ MW} = 1 \text{ megawatt}$). (a) Calculate the rate of temperature increase in degrees Celsius per second ($^\circ \text{C/s}$) if the mass of the reactor core is $1.60 \times 10^5 \text{ kg}$ and it has an average specific heat of $0.3349 \text{ kJ/kg} \cdot ^\circ \text{C}$. (b) How long would it take to obtain a temperature increase of 2000°C , which could cause some metals holding the radioactive materials to melt? (The initial rate of temperature increase would be greater than that calculated here because the heat transfer is concentrated in a smaller mass. Later, however, the temperature increase would slow down because the $500,000\text{-kg}$ steel containment vessel would also begin to heat up.)

Exercise:

Problem:

You leave a pastry in the refrigerator on a plate and ask your roommate to take it out before you get home so you can eat it at room temperature, the way you like it. Instead, your roommate plays video games for hours. When you return, you notice that the pastry is still cold, but the game console has become hot. Annoyed, and knowing that the pastry will not be good if it is microwaved, you warm up the pastry by unplugging the console and putting it in a clean trash bag (which acts as a perfect calorimeter) with the pastry on the plate. After a while, you find that the equilibrium temperature is a nice, warm 38.3°C . You know that the game console has a mass of 2.1 kg . Approximate it as having a uniform initial temperature of 45°C . The pastry has a mass of 0.16 kg and a specific heat of $3.0\text{ kJ}/(\text{kg} \cdot ^\circ\text{C})$, and is at a uniform initial temperature of 4.0°C . The plate is at the same temperature and has a mass of 0.24 kg and a specific heat of $0.90\text{ J}/(\text{kg} \cdot ^\circ\text{C})$. What is the specific heat of the console?

Solution:

$$1.7\text{ kJ}/(\text{kg} \cdot ^\circ\text{C})$$

Exercise:**Problem:**

Two solid spheres, A and B , made of the same material, are at temperatures of 0°C and 100°C , respectively. The spheres are placed in thermal contact in an ideal calorimeter, and they reach an equilibrium temperature of 20°C . Which is the bigger sphere? What is the ratio of their diameters?

Exercise:**Problem:**

In some countries, liquid nitrogen is used on dairy trucks instead of mechanical refrigerators. A 3.00-hour delivery trip requires 200 L of liquid nitrogen, which has a density of $808\text{ kg}/\text{m}^3$. (a) Calculate the heat transfer necessary to evaporate this amount of liquid nitrogen and raise its temperature to 3.00°C . (Use c_p and assume it is constant over the temperature range.) This value is the amount of cooling the liquid nitrogen supplies. (b) What is this heat transfer rate in kilowatt-hours? (c) Compare the amount of cooling obtained from melting an identical mass of 0°C ice with that from evaporating the liquid nitrogen.

Solution:

$$\text{a. } 1.57 \times 10^4\text{ kcal; b. } 18.3\text{ kW} \cdot \text{h; c. } 1.29 \times 10^4\text{ kcal}$$

Exercise:**Problem:**

Some gun fanciers make their own bullets, which involves melting lead and casting it into lead slugs. How much heat transfer is needed to raise the temperature and melt 0.500 kg of lead, starting from 25.0 °C?

Exercise:**Problem:**

A 0.800-kg iron cylinder at a temperature of 1.00×10^3 °C is dropped into an insulated chest of 1.00 kg of ice at its melting point. What is the final temperature, and how much ice has melted?

Solution:

6.3 °C. All of the ice melted.

Exercise:

Problem: Repeat the preceding problem with 2.00 kg of ice instead of 1.00 kg.

Exercise:**Problem:**

Repeat the preceding problem with 0.500 kg of ice, assuming that the ice is initially in a copper container of mass 1.50 kg in equilibrium with the ice.

Solution:

63.9 °C, all the ice melted

Exercise:**Problem:**

A 30.0-g ice cube at its melting point is dropped into an aluminum calorimeter of mass 100.0 g in equilibrium at 24.0 °C with 300.0 g of an unknown liquid. The final temperature is 4.0 °C. What is the heat capacity of the liquid?

Exercise:

Problem:

(a) Calculate the rate of heat conduction through a double-paned window that has a 1.50-m^2 area and is made of two panes of 0.800-cm -thick glass separated by a 1.00-cm air gap. The inside surface temperature is 15.0°C , while that on the outside is -10.0°C . (*Hint:* There are identical temperature drops across the two glass panes. First find these and then the temperature drop across the air gap. This problem ignores the increased heat transfer in the air gap due to convection.) (b) Calculate the rate of heat conduction through a 1.60-cm -thick window of the same area and with the same temperatures. Compare your answer with that for part (a).

Solution:

a. 83 W ; b. $1.97 \times 10^3\text{ W}$; The single-pane window has a rate of heat conduction equal to $1969/83$, or 24 times that of a double-pane window.

Exercise:**Problem:**

(a) An exterior wall of a house is 3 m tall and 10 m wide. It consists of a layer of drywall with an R factor of 0.56 , a layer 3.5 inches thick filled with fiberglass batts, and a layer of insulated siding with an R factor of 2.6 . The wall is built so well that there are no leaks of air through it. When the inside of the wall is at 22°C and the outside is at -2°C , what is the rate of heat flow through the wall? (b) More realistically, the 3.5 -inch space also contains 2-by-4 studs—wooden boards 1.5 inches by 3.5 inches oriented so that 3.5 -inch dimension extends from the drywall to the siding. They are “on 16-inch centers,” that is, the centers of the studs are 16 inches apart. What is the heat current in this situation? Don’t worry about one stud more or less.

Exercise:**Problem:**

For the human body, what is the rate of heat transfer by conduction through the body’s tissue with the following conditions: the tissue thickness is 3.00 cm , the difference in temperature is 2.00°C , and the skin area is 1.50 m^2 . How does this compare with the average heat transfer rate to the body resulting from an energy intake of about 2400 kcal per day? (No exercise is included.)

Solution:

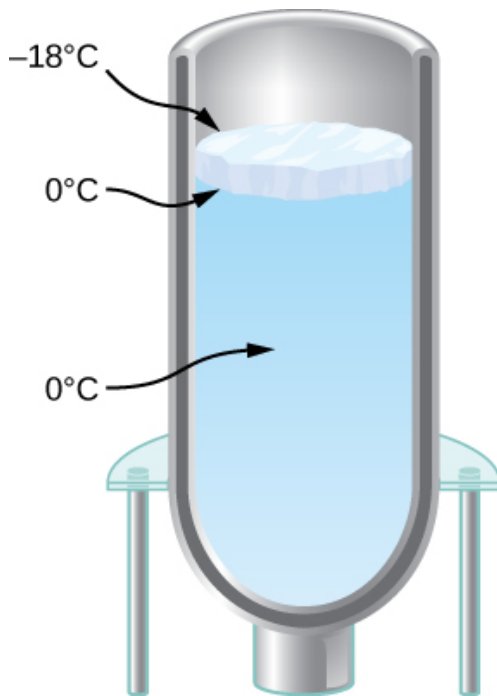
The rate of heat transfer by conduction is 20.0 W . On a daily basis, this is $1,728\text{ kJ/day}$. Daily food intake is $2400\text{ kcal/d} \times 4186\text{ J/kcal} = 10,050\text{ kJ/day}$. So

only 17.2% of energy intake goes as heat transfer by conduction to the environment at this ΔT .

Exercise:

Problem:

You have a Dewar flask (a laboratory vacuum flask) that has an open top and straight sides, as shown below. You fill it with water and put it into the freezer. It is effectively a perfect insulator, blocking all heat transfer, except on the top. After a time, ice forms on the surface of the water. The liquid water and the bottom surface of the ice, in contact with the liquid water, are at 0°C . The top surface of the ice is at the same temperature as the air in the freezer, -18°C . Set the rate of heat flow through the ice equal to the rate of loss of heat of fusion as the water freezes. When the ice layer is 0.700 cm thick, find the rate in m/s at which the ice is thickening.



Exercise:

Problem:

An infrared heater for a sauna has a surface area of 0.050 m^2 and an emissivity of 0.84. What temperature must it run at if the required power is 360 W? Neglect the temperature of the environment.

Solution:

620 K

Exercise:**Problem:**

- (a) Determine the power of radiation from the Sun by noting that the intensity of the radiation at the distance of Earth is 1370 W/m^2 . *Hint:* That intensity will be found everywhere on a spherical surface with radius equal to that of Earth's orbit.
- (b) Assuming that the Sun's temperature is 5780 K and that its emissivity is 1, find its radius.

Challenge Problems**Exercise:****Problem:**

A pendulum is made of a rod of length L and negligible mass, but capable of thermal expansion, and a weight of negligible size. (a) Show that when the temperature increases by dT , the period of the pendulum increases by a fraction $\alpha L dT / 2$. (b) A clock controlled by a brass pendulum keeps time correctly at 10°C . If the room temperature is 30°C , does the clock run faster or slower? What is its error in seconds per day?

Solution:

Denoting the period by P , we know $P = 2\pi\sqrt{L/g}$. When the temperature increases by dT , the length increases by $\alpha L dT$. Then the new length is a.

$$P = 2\pi\sqrt{\frac{L+\alpha L dT}{g}} = 2\pi\sqrt{\frac{L}{g}(1 + \alpha dT)} = 2\pi\sqrt{\frac{L}{g}} \left(1 + \frac{1}{2}\alpha dT\right) = P \left(1 + \frac{1}{2}\alpha dT\right)$$

by the binomial expansion. b. The clock runs slower, as its new period is 1.00019 s . It loses 16.4 s per day.

Exercise:**Problem:**

At temperatures of a few hundred kelvins the specific heat capacity of copper approximately follows the empirical formula $c = \alpha + \beta T + \delta T^{-2}$, where $\alpha = 349 \text{ J/kg} \cdot \text{K}$, $\beta = 0.107 \text{ J/kg} \cdot \text{K}^2$, and $\delta = 4.58 \times 10^5 \text{ J} \cdot \text{kg} \cdot \text{K}$. How much heat is needed to raise the temperature of a 2.00-kg piece of copper from 20°C to 250°C ?

Exercise:

Problem:

In a calorimeter of negligible heat capacity, 200 g of steam at 150°C and 100 g of ice at -40°C are mixed. The pressure is maintained at 1 atm. What is the final temperature, and how much steam, ice, and water are present?

Solution:

The amount of heat to melt the ice and raise it to 100°C is not enough to condense the steam, but it is more than enough to lower the steam's temperature by 50°C , so the final state will consist of steam and liquid water in equilibrium, and the final temperature is 100°C ; 9.5 g of steam condenses, so the final state contains 49.5 g of steam and 40.5 g of liquid water.

Exercise:**Problem:**

An astronaut performing an extra-vehicular activity (space walk) shaded from the Sun is wearing a spacesuit that can be approximated as perfectly white ($e = 0$) except for a $5\text{ cm} \times 8\text{ cm}$ patch in the form of the astronaut's national flag. The patch has emissivity 0.300. The spacesuit under the patch is 0.500 cm thick, with a thermal conductivity $k = 0.0600\text{ W/m}^\circ\text{C}$, and its inner surface is at a temperature of 20.0°C . What is the temperature of the patch, and what is the rate of heat loss through it? Assume the patch is so thin that its outer surface is at the same temperature as the outer surface of the spacesuit under it. Also assume the temperature of outer space is 0 K. You will get an equation that is very hard to solve in closed form, so you can solve it numerically with a graphing calculator, with software, or even by trial and error with a calculator.

Exercise:**Problem:**

The goal in this problem is to find the growth of an ice layer as a function of time. Call the thickness of the ice layer L . (a) Derive an equation for dL/dt in terms of L , the temperature T above the ice, and the properties of ice (which you can leave in symbolic form instead of substituting the numbers). (b) Solve this differential equation assuming that at $t = 0$, you have $L = 0$. If you have studied differential equations, you will know a technique for solving equations of this type: manipulate the equation to get dL/dt multiplied by a (very simple) function of L on one side, and integrate both sides with respect to time. Alternatively, you may be able to use your knowledge of the derivatives of various functions to guess the solution, which has a simple dependence on t . (c) Will the water eventually freeze to the bottom of the flask?

Solution:

a. $dL/dT = kT/\rho L$; b. $L = \sqrt{2kTt/\rho L_f}$; c. yes

Exercise:**Problem:**

As the very first rudiment of climatology, estimate the temperature of Earth. Assume it is a perfect sphere and its temperature is uniform. Ignore the greenhouse effect. Thermal radiation from the Sun has an intensity (the “solar constant” S) of about 1370 W/m^2 at the radius of Earth’s orbit. (a) Assuming the Sun’s rays are parallel, what area must S be multiplied by to get the total radiation intercepted by Earth? It will be easiest to answer in terms of Earth’s radius, R . (b) Assume that Earth reflects about 30% of the solar energy it intercepts. In other words, Earth has an albedo with a value of $A = 0.3$. In terms of S , A , and R , what is the rate at which Earth absorbs energy from the Sun? (c) Find the temperature at which Earth radiates energy at the same rate. Assume that at the infrared wavelengths where it radiates, the emissivity e is 1. Does your result show that the greenhouse effect is important? (d) How does your answer depend on the the area of Earth?

Exercise:**Problem:**

Let’s stop ignoring the greenhouse effect and incorporate it into the previous problem in a very rough way. Assume the atmosphere is a single layer, a spherical shell around Earth, with an emissivity $e = 0.77$ (chosen simply to give the right answer) at infrared wavelengths emitted by Earth and by the atmosphere. However, the atmosphere is transparent to the Sun’s radiation (that is, assume the radiation is at visible wavelengths with no infrared), so the Sun’s radiation reaches the surface. The greenhouse effect comes from the difference between the atmosphere’s transmission of visible light and its rather strong absorption of infrared. Note that the atmosphere’s radius is not significantly different from Earth’s, but since the atmosphere is a layer above Earth, it emits radiation both upward and downward, so it has twice Earth’s area. There are three radiative energy transfers in this problem: solar radiation absorbed by Earth’s surface; infrared radiation from the surface, which is absorbed by the atmosphere according to its emissivity; and infrared radiation from the atmosphere, half of which is absorbed by Earth and half of which goes out into space. Apply the method of the previous problem to get an equation for Earth’s surface and one for the atmosphere, and solve them for the two unknown temperatures, surface and atmosphere.

- a. In terms of Earth’s radius, the constant σ , and the unknown temperature T_s of the surface, what is the power of the infrared radiation from the surface?

- b. What is the power of Earth's radiation absorbed by the atmosphere?
- c. In terms of the unknown temperature T_e of the atmosphere, what is the power radiated from the atmosphere?
- d. Write an equation that says the power of the radiation the atmosphere absorbs from Earth equals the power of the radiation it emits.
- e. Half of the power radiated by the atmosphere hits Earth. Write an equation that says that the power Earth absorbs from the atmosphere and the Sun equals the power that it emits.
- f. Solve your two equations for the unknown temperature of Earth.
For steps that make this model less crude, see for example the [lectures](#) by Paul O'Gorman.

Solution:

a. $\sigma (\pi R^2) T_s^4$; b. $e\sigma\pi R^2 T_s^4$; c. $2e\sigma\pi R^2 T_e^4$; d. $T_s^4 = 2T_e^4$; e. $e\sigma T_s^4 + \frac{1}{4}(1 - A)S = \sigma T_s^4$; f. 288 K

Glossary

conduction

heat transfer through stationary matter by physical contact

convection

heat transfer by the macroscopic movement of fluid

emissivity

measure of how well an object radiates

greenhouse effect

warming of the earth that is due to gases such as carbon dioxide and methane that absorb infrared radiation from Earth's surface and reradiate it in all directions, thus sending some of it back toward Earth

net rate of heat transfer by radiation

$$P_{\text{net}} = \sigma e A (T_2^4 - T_1^4)$$

radiation

energy transferred by electromagnetic waves directly as a result of a temperature difference

rate of conductive heat transfer

rate of heat transfer from one material to another

Stefan-Boltzmann law of radiation

$P = \sigma A e T^4$, where $\sigma = 5.67 \times 10^{-8} \text{ J/s} \cdot \text{m}^2 \cdot \text{K}^4$ is the Stefan-Boltzmann constant, A is the surface area of the object, T is the absolute temperature, and e is the emissivity

thermal conductivity

property of a material describing its ability to conduct heat

Introduction

class="introduction"

A volcanic eruption releases tons of gas and dust into the atmosphere. Most of the gas is water vapor, but several other gases are common, including greenhouse gases such as carbon dioxide and acidic pollutants such as sulfur dioxide.

However, the emission of volcanic gas is not all bad: Many geologists believe that in the earliest stages of Earth's formation, volcanic emissions formed the early atmosphere. (credit: modification of work by "Boaworm"/Wikimedia Commons)



Gases are literally all around us—the air that we breathe is a mixture of gases. Other gases include those that make breads and cakes soft, those that make drinks fizzy, and those that burn to heat many homes. Engines and refrigerators depend on the behaviors of gases, as we will see in later chapters.

As we discussed in the preceding chapter, the study of heat and temperature is part of an area of physics known as thermodynamics, in which we require a system to be *macroscopic*, that is, to consist of a huge number (such as 10^{23}) of molecules. We begin by considering some macroscopic properties of gases: volume, pressure, and temperature. The simple model of a hypothetical “ideal gas” describes these properties of a gas very accurately under many conditions. We move from the ideal gas model to a more widely applicable approximation, called the Van der Waals model.

To understand gases even better, we must also look at them on the *microscopic* scale of molecules. In gases, the molecules interact weakly, so the microscopic behavior of gases is relatively simple, and they serve as a good introduction to systems of many molecules. The molecular model of gases is called the kinetic theory of gases and is one of the classic examples of a molecular model that explains everyday behavior.

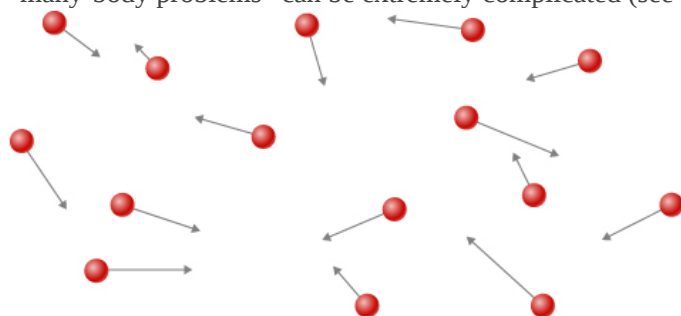
Molecular Model of an Ideal Gas

By the end of this section, you will be able to:

- Apply the ideal gas law to situations involving the pressure, volume, temperature, and the number of molecules of a gas
- Use the unit of moles in relation to numbers of molecules, and molecular and macroscopic masses
- Explain the ideal gas law in terms of moles rather than numbers of molecules
- Apply the van der Waals gas law to situations where the ideal gas law is inadequate

In this section, we explore the thermal behavior of gases. Our word “gas” comes from the Flemish word meaning “chaos,” first used for vapors by the seventeenth-century chemist J. B. van Helmont. The term was more appropriate than he knew, because gases consist of molecules moving and colliding with each other at random. This randomness makes the connection between the microscopic and macroscopic domains simpler for gases than for liquids or solids.

How do gases differ from solids and liquids? Under ordinary conditions, such as those of the air around us, the difference is that the molecules of gases are much farther apart than those of solids and liquids. Because the typical distances between molecules are large compared to the size of a molecule, as illustrated in [\[link\]](#), the forces between them are considered negligible, except when they come into contact with each other during collisions. Also, at temperatures well above the boiling temperature, the motion of molecules is fast, and the gases expand rapidly to occupy all of the accessible volume. In contrast, in liquids and solids, molecules are closer together, and the behavior of molecules in liquids and solids is highly constrained by the molecules’ interactions with one another. The macroscopic properties of such substances depend strongly on the forces between the molecules, and since many molecules are interacting, the resulting “many-body problems” can be extremely complicated (see [Condensed Matter Physics](#)).

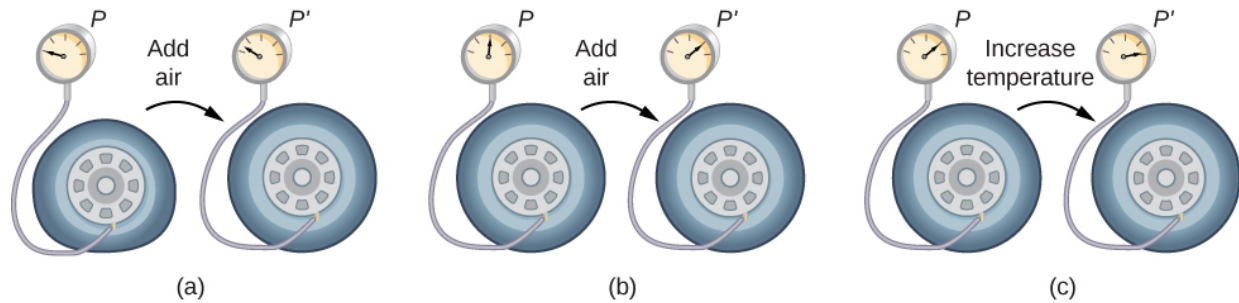


Atoms and molecules in a gas are typically widely separated. Because the forces between them are quite weak at these distances, the properties of a gas depend more on the number of atoms per unit volume and on temperature than on the type of atom.

The Gas Laws

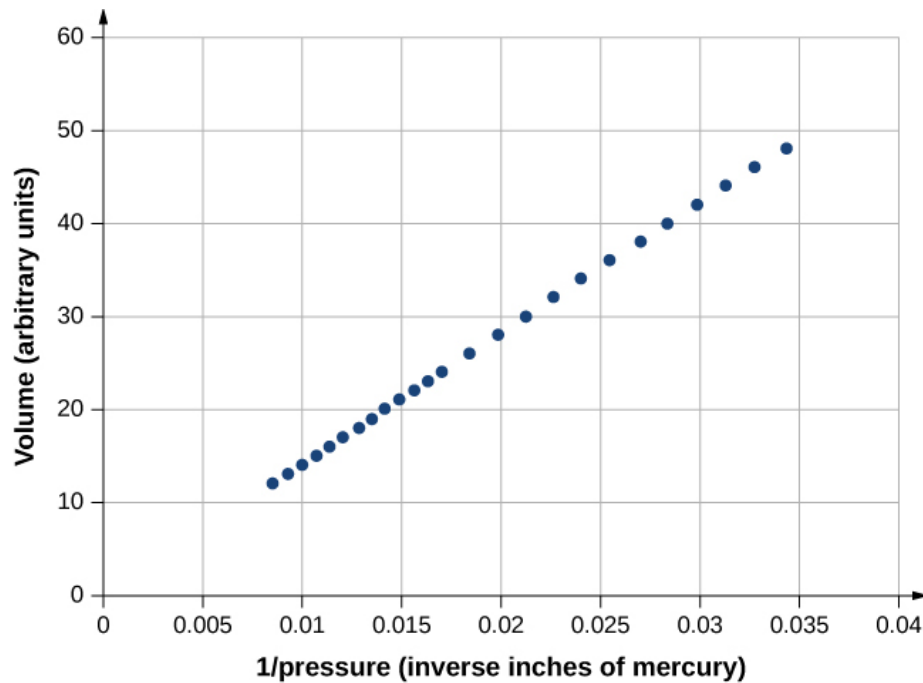
In the previous chapter, we saw one consequence of the large intermolecular spacing in gases: Gases are easily compressed. [\[link\]](#) shows that gases have larger coefficients of volume expansion than either solids or liquids. These large coefficients mean that gases expand and contract very rapidly with temperature changes. We also saw (in the section on thermal expansion) that most gases expand at the same rate or have the same coefficient of volume expansion, β . This raises a question: Why do all gases act in nearly the same way, when all the various liquids and solids have widely varying expansion rates?

To study how the pressure, temperature, and volume of a gas relate to one another, consider what happens when you pump air into a deflated car tire. The tire's volume first increases in direct proportion to the amount of air injected, without much increase in the tire pressure. Once the tire has expanded to nearly its full size, the tire's walls limit its volume expansion. If we continue to pump air into the tire, the pressure increases. When the car is driven and the tires flex, their temperature increases, and therefore the pressure increases even further ([link](#)).



(a) When air is pumped into a deflated tire, its volume first increases without much increase in pressure. (b) When the tire is filled to a certain point, the tire walls resist further expansion, and the pressure increases with more air. (c) Once the tire is inflated, its pressure increases with temperature.

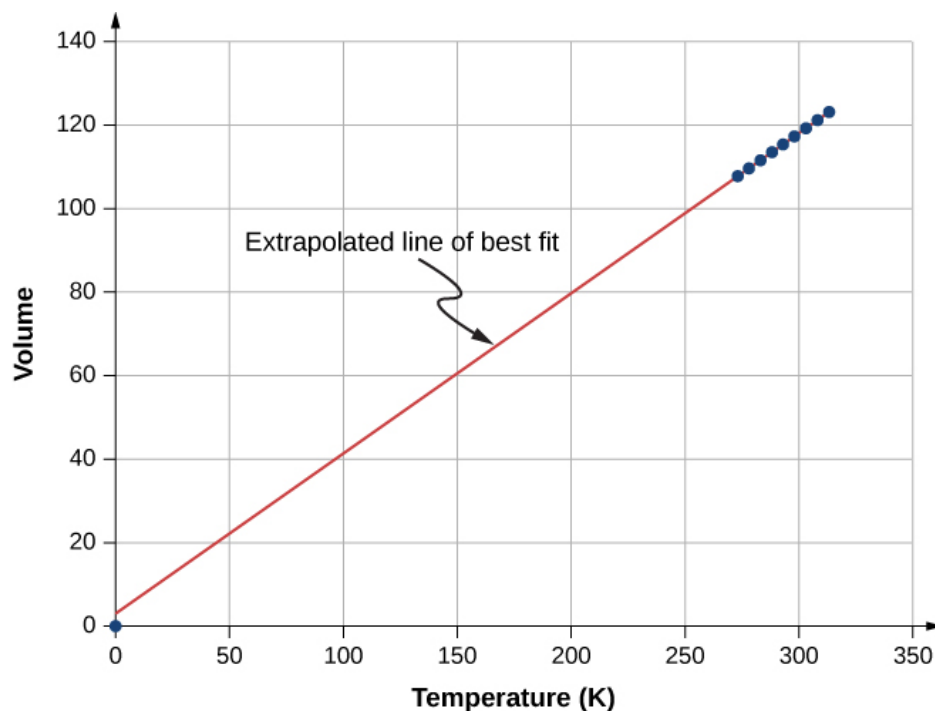
[link](#) shows data from the experiments of Robert Boyle (1627–1691), illustrating what is now called Boyle's law: At constant temperature and number of molecules, the absolute pressure of a gas and its volume are inversely proportional. (Recall from [Fluid Mechanics](#) that the absolute pressure is the true pressure and the gauge pressure is the absolute pressure minus the ambient pressure, typically atmospheric pressure.) The graph in [link](#) displays this relationship as an inverse proportionality of volume to pressure.



Robert Boyle and his assistant found that volume and pressure are inversely proportional. Here their data are plotted as V versus $1/p$; the linearity of the graph shows the inverse proportionality. The number shown as the volume is actually the height in inches of air in a cylindrical glass tube. The actual volume was that height multiplied by the cross-sectional area of the tube, which Boyle did not publish. The data are from Boyle's book *A Defence of the Doctrine Touching the Spring and Weight of the Air...*, p. 60.[\[footnote\]](#)

<http://bvpb.mcu.es/en/consulta/registro.cmd?id=406806>

[\[link\]](#) shows experimental data illustrating what is called Charles's law, after Jacques Charles (1746–1823). Charles's law states that at constant pressure and number of molecules, the volume of a gas is proportional to its absolute temperature.



Experimental data showing that at constant pressure, volume is approximately proportional to temperature. The best-fit line passes approximately through the origin. [\[footnote\]](http://chemed.chem.purdue.edu/genchem/history/charles.html)
<http://chemed.chem.purdue.edu/genchem/history/charles.html>

Similar is Amonton's or Gay-Lussac's law, which states that at constant volume and number of molecules, the pressure is proportional to the temperature. That law is the basis of the constant-volume gas thermometer, discussed in the previous chapter. (The histories of these laws and the appropriate credit for them are more complicated than can be discussed here.)

It is known experimentally that for gases at low density (such that their molecules occupy a negligible fraction of the total volume) and at temperatures well above the boiling point, these proportionalities hold to a good approximation. Not surprisingly, with the other quantities held constant, either pressure or volume is proportional to the number of molecules. More surprisingly, when the proportionalities are combined into a single equation, the constant of proportionality is independent of the composition of the gas. The resulting equation for all gases applies in the limit of low density and high temperature; it's the same for oxygen as for helium or uranium hexafluoride. A gas at that limit is called an **ideal gas**; it obeys the **ideal gas law**, which is also called the equation of state of an ideal gas.

Note:

Ideal Gas Law

The ideal gas law states that

Equation:

$$pV = Nk_{\text{B}}T,$$

where p is the absolute pressure of a gas, V is the volume it occupies, N is the number of molecules in the gas, and T is its absolute temperature.

The constant k_B is called the **Boltzmann constant** in honor of the Austrian physicist Ludwig Boltzmann (1844–1906) and has the value

Equation:

$$k_B = 1.38 \times 10^{-23} \text{ J/K}.$$

The ideal gas law describes the behavior of any real gas when its density is low enough or its temperature high enough that it is far from liquefaction. This encompasses many practical situations. In the next section, we'll see why it's independent of the type of gas.

In many situations, the ideal gas law is applied to a sample of gas with a constant number of molecules; for instance, the gas may be in a sealed container. If N is constant, then solving for N shows that pV/T is constant. We can write that fact in a convenient form:

Note:

Equation:

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2},$$

where the subscripts 1 and 2 refer to any two states of the gas at different times. Again, the temperature must be expressed in kelvin and the pressure must be absolute pressure, which is the sum of gauge pressure and atmospheric pressure.

Example:

Calculating Pressure Changes Due to Temperature Changes

Suppose your bicycle tire is fully inflated, with an absolute pressure of $7.00 \times 10^5 \text{ Pa}$ (a gauge pressure of just under 90.0 lb/in.^2) at a temperature of 18.0°C . What is the pressure after its temperature has risen to 35.0°C on a hot day? Assume there are no appreciable leaks or changes in volume.

Strategy

The pressure in the tire is changing only because of changes in temperature. We know the initial pressure $p_0 = 7.00 \times 10^5 \text{ Pa}$, the initial temperature $T_0 = 18.0^\circ \text{C}$, and the final temperature $T_f = 35.0^\circ \text{C}$. We must find the final pressure p_f . Since the number of molecules is constant, we can use the equation

Equation:

$$\frac{p_f V_f}{T_f} = \frac{p_0 V_0}{T_0}.$$

Since the volume is constant, V_f and V_0 are the same and they divide out. Therefore,

Equation:

$$\frac{p_f}{T_f} = \frac{p_0}{T_0}.$$

We can then rearrange this to solve for p_f :

Equation:

$$p_f = p_0 \frac{T_f}{T_0},$$

where the temperature must be in kelvin.

Solution

1. Convert temperatures from degrees Celsius to kelvin

Equation:

$$T_0 = (18.0 + 273)\text{K} = 291 \text{ K},$$

Equation:

$$T_f = (35.0 + 273)\text{K} = 308 \text{ K}.$$

2. Substitute the known values into the equation,

Equation:

$$p_f = p_0 \frac{T_f}{T_0} = 7.00 \times 10^5 \text{ Pa} \left(\frac{308 \text{ K}}{291 \text{ K}} \right) = 7.41 \times 10^5 \text{ Pa}.$$

Significance

The final temperature is about 6 % greater than the original temperature, so the final pressure is about 6 % greater as well. Note that *absolute pressure* (see [Fluid Mechanics](#)) and *absolute temperature* (see [Temperature and Heat](#)) must be used in the ideal gas law.

Example:

Calculating the Number of Molecules in a Cubic Meter of Gas

How many molecules are in a typical object, such as gas in a tire or water in a glass? This calculation can give us an idea of how large N typically is. Let's calculate the number of molecules in the air that a typical healthy young adult inhales in one breath, with a volume of 500 mL, at *standard temperature and pressure* (STP), which is defined as 0 °C and atmospheric pressure. (Our young adult is apparently outside in winter.)

Strategy

Because pressure, volume, and temperature are all specified, we can use the ideal gas law, $pV = Nk_B T$, to find N .

Solution

1. Identify the knowns.

Equation:

$$T = 0^\circ \text{C} = 273 \text{ K}, p = 1.01 \times 10^5 \text{ Pa}, V = 500 \text{ mL} = 5 \times 10^{-4} \text{ m}^3, k_B = 1.38 \times 10^{-23} \text{ J/K}$$

2. Substitute the known values into the equation and solve for N .

Equation:

$$N = \frac{pV}{k_B T} = \frac{(1.01 \times 10^5 \text{ Pa}) (5 \times 10^{-4} \text{ m}^3)}{(1.38 \times 10^{-23} \text{ J/K}) (273 \text{ K})} = 1.34 \times 10^{22} \text{ molecules}$$

Significance

N is huge, even in small volumes. For example, 1 cm^3 of a gas at STP contains 2.68×10^{19} molecules. Once again, note that our result for N is the same for all types of gases, including mixtures.

As we observed in the chapter on fluid mechanics, pascals are N/m^2 , so $\text{Pa} \cdot \text{m}^3 = \text{N} \cdot \text{m} = \text{J}$. Thus, our result for N is dimensionless, a pure number that could be obtained by counting (in principle) rather than measuring. As it is the number of molecules, we put “molecules” after the number, keeping in mind that it is an aid to communication rather than a unit.

Moles and Avogadro’s Number

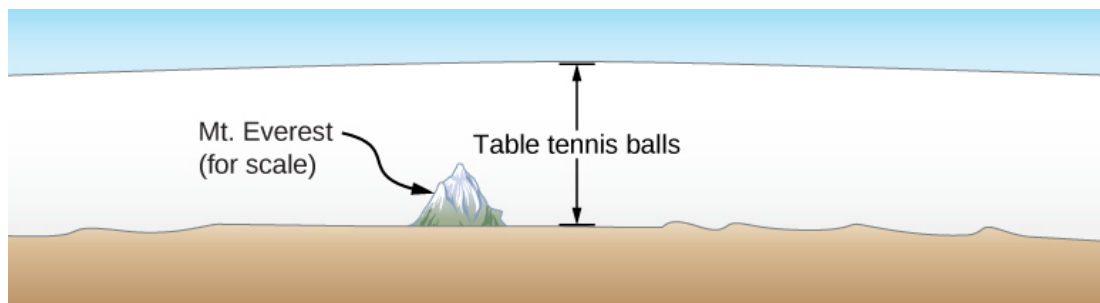
It is often convenient to measure the amount of substance with a unit on a more human scale than molecules. The SI unit for this purpose was developed by the Italian scientist Amedeo Avogadro (1776–1856). (He worked from the hypothesis that equal volumes of gas at equal pressure and temperature contain equal numbers of molecules, independent of the type of gas. As mentioned above, this hypothesis has been confirmed when the ideal gas approximation applies.) A **mole** (abbreviated mol) is defined as the amount of any substance that contains as many molecules as there are atoms in exactly 12 grams (0.012 kg) of carbon-12. (Technically, we should say “formula units,” not “molecules,” but this distinction is irrelevant for our purposes.) The number of molecules in one mole is called **Avogadro’s number** (N_A), and the value of Avogadro’s number is now known to be

Equation:

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}.$$

We can now write $N = N_A n$, where n represents the number of moles of a substance.

Avogadro’s number relates the mass of an amount of substance in grams to the number of protons and neutrons in an atom or molecule (12 for a carbon-12 atom), which roughly determine its mass. It’s natural to define a unit of mass such that the mass of an atom is approximately equal to its number of neutrons and protons. The unit of that kind accepted for use with the SI is the *unified atomic mass unit* (u), also called the *dalton*. Specifically, a carbon-12 atom has a mass of exactly 12 u, so that its molar mass M in grams per mole is numerically equal to the mass of one carbon-12 atom in u. That equality holds for any substance. In other words, N_A is not only the conversion from numbers of molecules to moles, but it is also the conversion from u to grams: $6.02 \times 10^{23} \text{ u} = 1 \text{ g}$. See [\[link\]](#).



How big is a mole? On a macroscopic level, Avogadro's number of table tennis balls would cover Earth to a depth of about 40 km.

Now letting m_s stand for the mass of a sample of a substance, we have $m_s = nM$. Letting m stand for the mass of a molecule, we have $M = N_A m$.

Note:

Exercise:

Problem:

Check Your Understanding The recommended daily amount of vitamin B₃ or niacin, C₆H₅O₂, for women who are not pregnant or nursing, is 14 mg. Find the number of molecules of niacin in that amount.

Solution:

We first need to calculate the molar mass (the mass of one mole) of niacin. To do this, we must multiply the number of atoms of each element in the molecule by the element's molar mass.

$$(6 \text{ mol of carbon}) (12.0 \text{ g/mol}) + (5 \text{ mol hydrogen}) (1.0 \text{ g/mol}) \\ + (1 \text{ mol nitrogen}) (14 \text{ g/mol}) + (2 \text{ mol oxygen}) (16.0 \text{ g/mol}) = 123 \text{ g/mol}$$

Then we need to calculate the number of moles in 14 mg.

$$\left(\frac{14 \text{ mg}}{123 \text{ g/mol}} \right) \left(\frac{1 \text{ g}}{1000 \text{ mg}} \right) = 1.14 \times 10^{-4} \text{ mol.}$$

Then, we use Avogadro's number to calculate the number of molecules:

$$N = nN_A = (1.14 \times 10^{-4} \text{ mol}) (6.02 \times 10^{23} \text{ molecules/mol}) = 6.85 \times 10^{19} \text{ molecules.}$$

Note:

Exercise:

Problem:

Check Your Understanding The density of air in a classroom ($p = 1.00 \text{ atm}$ and $T = 20^\circ \text{C}$) is 1.28 kg/m^3 . At what pressure is the density 0.600 kg/m^3 if the temperature is kept constant?

Solution:

The density of a gas is equal to a constant, the average molecular mass, times the number density N/V . From the ideal gas law, $pV = Nk_B T$, we see that $N/V = p/k_B T$. Therefore, at constant temperature, if the density and, consequently, the number density are reduced by half, the pressure must also be reduced by half, and $p_f = 0.500$ atm.

The Ideal Gas Law Restated using Moles

A very common expression of the ideal gas law uses the number of moles in a sample, n , rather than the number of molecules, N . We start from the ideal gas law,

Equation:

$$pV = Nk_B T,$$

and multiply and divide the right-hand side of the equation by Avogadro's number N_A . This gives us

Equation:

$$pV = \frac{N}{N_A} N_A k_B T.$$

Note that $n = N/N_A$ is the number of moles. We define the **universal gas constant** as $R = N_A k_B$, and obtain the ideal gas law in terms of moles.

Note:

Ideal Gas Law (in terms of moles)

In terms of number of moles n , the ideal gas law is written as

Equation:

$$pV = nRT.$$

In SI units,

Equation:

$$R = N_A k_B = (6.02 \times 10^{23} \text{ mol}^{-1}) \left(1.38 \times 10^{-23} \frac{\text{J}}{\text{K}} \right) = 8.31 \frac{\text{J}}{\text{mol} \cdot \text{K}}.$$

In other units,

Equation:

$$R = 1.99 \frac{\text{cal}}{\text{mol} \cdot \text{K}} = 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}.$$

You can use whichever value of R is most convenient for a particular problem.

Example:

Density of Air at STP and in a Hot Air Balloon

Calculate the density of dry air (a) under standard conditions and (b) in a hot air balloon at a temperature of 120 °C. Dry air is approximately 78 % N₂, 21 % O₂, and 1 % Ar.

Strategy and Solution

- a. We are asked to find the density, or mass per cubic meter. We can begin by finding the molar mass. If we have a hundred molecules, of which 78 are nitrogen, 21 are oxygen, and 1 is argon, the average molecular mass is $\frac{78 m_{N_2} + 21 m_{O_2} + m_{Ar}}{100}$, or the mass of each constituent multiplied by its percentage. The same applies to the molar mass, which therefore is

Equation:

$$M = 0.78 M_{N_2} + 0.21 M_{O_2} + 0.01 M_{Ar} = 29.0 \text{ g/mol.}$$

Now we can find the number of moles per cubic meter. We use the ideal gas law in terms of moles, $pV = nRT$, with $p = 1.00 \text{ atm}$, $T = 273 \text{ K}$, $V = 1 \text{ m}^3$, and $R = 8.31 \text{ J/mol} \cdot \text{K}$. The most convenient choice for R in this case is $R = 8.31 \text{ J/mol} \cdot \text{K}$ because the known quantities are in SI units:

Equation:

$$n = \frac{pV}{RT} = \frac{(1.01 \times 10^5 \text{ Pa})(1 \text{ m}^3)}{(8.31 \text{ J/mol} \cdot \text{K})(273 \text{ K})} = 44.5 \text{ mol.}$$

Then, the mass m_s of that air is

Equation:

$$m_s = nM = (44.5 \text{ mol})(29.0 \text{ g/mol}) = 1290 \text{ g} = 1.29 \text{ kg.}$$

Finally the density of air at STP is

Equation:

$$\rho = \frac{m_s}{V} = \frac{1.29 \text{ kg}}{1 \text{ m}^3} = 1.29 \text{ kg/m}^3.$$

- b. The air pressure inside the balloon is still 1 atm because the bottom of the balloon is open to the atmosphere. The calculation is the same except that we use a temperature of 120 °C, which is 393 K. We can repeat the calculation in (a), or simply observe that the density is proportional to the number of moles, which is inversely proportional to the temperature. Then using the subscripts 1 for air at STP and 2 for the hot air, we have

Equation:

$$\rho_2 = \frac{T_1}{T_2} \rho_1 = \frac{273 \text{ K}}{393 \text{ K}} (1.29 \text{ kg/m}^3) = 0.896 \text{ kg/m}^3.$$

Significance

Using the methods of [Archimedes' Principle and Buoyancy](#), we can find that the net force on 2200 m³ of air at 120 °C is $F_b - F_g = \rho_{\text{atmosphere}} Vg - \rho_{\text{hot air}} Vg = 8.49 \times 10^3 \text{ N}$, or enough to lift about 867 kg. The mass density and molar density of air at STP, found above, are often useful numbers. From the molar density, we can easily determine another useful number, the volume of a mole of any ideal gas at STP, which is 22.4 L.

Note:**Exercise:****Problem:**

Check Your Understanding Liquids and solids have densities on the order of 1000 times greater than gases. Explain how this implies that the distances between molecules in gases are on the order of 10 times greater than the size of their molecules.

Solution:

Density is mass per unit volume, and volume is proportional to the size of a body (such as the radius of a sphere) cubed. So if the distance between molecules increases by a factor of 10, then the volume occupied increases by a factor of 1000, and the density decreases by a factor of 1000. Since we assume molecules are in contact in liquids and solids, the distance between their centers is on the order of their typical size, so the distance in gases is on the order of 10 times as great.

The ideal gas law is closely related to energy: The units on both sides of the equation are joules. The right-hand side of the ideal gas law equation is $Nk_{\text{B}}T$. This term is roughly the total translational kinetic energy (which, when discussing gases, refers to the energy of translation of a molecule, not that of vibration of its atoms or rotation) of N molecules at an absolute temperature T , as we will see formally in the next section. The left-hand side of the ideal gas law equation is pV . As mentioned in the example on the number of molecules in an ideal gas, pressure multiplied by volume has units of energy. The energy of a gas can be changed when the gas does work as it increases in volume, something we explored in the preceding chapter, and the amount of work is related to the pressure. This is the process that occurs in gasoline or steam engines and turbines, as we'll see in the next chapter.

Note:**Problem-Solving Strategy: The Ideal Gas Law**

Step 1. Examine the situation to determine that an ideal gas is involved. Most gases are nearly ideal unless they are close to the boiling point or at pressures far above atmospheric pressure.

Step 2. Make a list of what quantities are given or can be inferred from the problem as stated (identify the known quantities).

Step 3. Identify exactly what needs to be determined in the problem (identify the unknown quantities). A written list is useful.

Step 4. Determine whether the number of molecules or the number of moles is known or asked for to decide whether to use the ideal gas law as $pV = Nk_{\text{B}}T$, where N is the number of molecules, or $pV = nRT$, where n is the number of moles.

Step 5. Convert known values into proper SI units (K for temperature, Pa for pressure, m^3 for volume, molecules for N , and moles for n). If the units of the knowns are consistent with one of the non-SI values of R , you can leave them in those units. Be sure to use absolute temperature and absolute pressure.

Step 6. Solve the ideal gas law for the quantity to be determined (the unknown quantity). You may need to take a ratio of final states to initial states to eliminate the unknown quantities that are kept fixed.

Step 7. Substitute the known quantities, along with their units, into the appropriate equation and obtain numerical solutions complete with units.

Step 8. Check the answer to see if it is reasonable: Does it make sense?

The Van der Waals Equation of State

We have repeatedly noted that the ideal gas law is an approximation. How can it be improved upon? The **van der Waals equation of state** (named after the Dutch physicist Johannes van der Waals, 1837–1923) improves it by taking into account two factors. First, the attractive forces between molecules, which are stronger at higher density and reduce the pressure, are taken into account by adding to the pressure a term equal to the square of the molar density multiplied by a positive coefficient a . Second, the volume of the molecules is represented by a positive constant b , which can be thought of as the volume of a mole of molecules. This is subtracted from the total volume to give the remaining volume that the molecules can move in. The constants a and b are determined experimentally for each gas. The resulting equation is

Note:
Equation:

$$\left[p + a \left(\frac{n}{V} \right)^2 \right] (V - nb) = nRT.$$

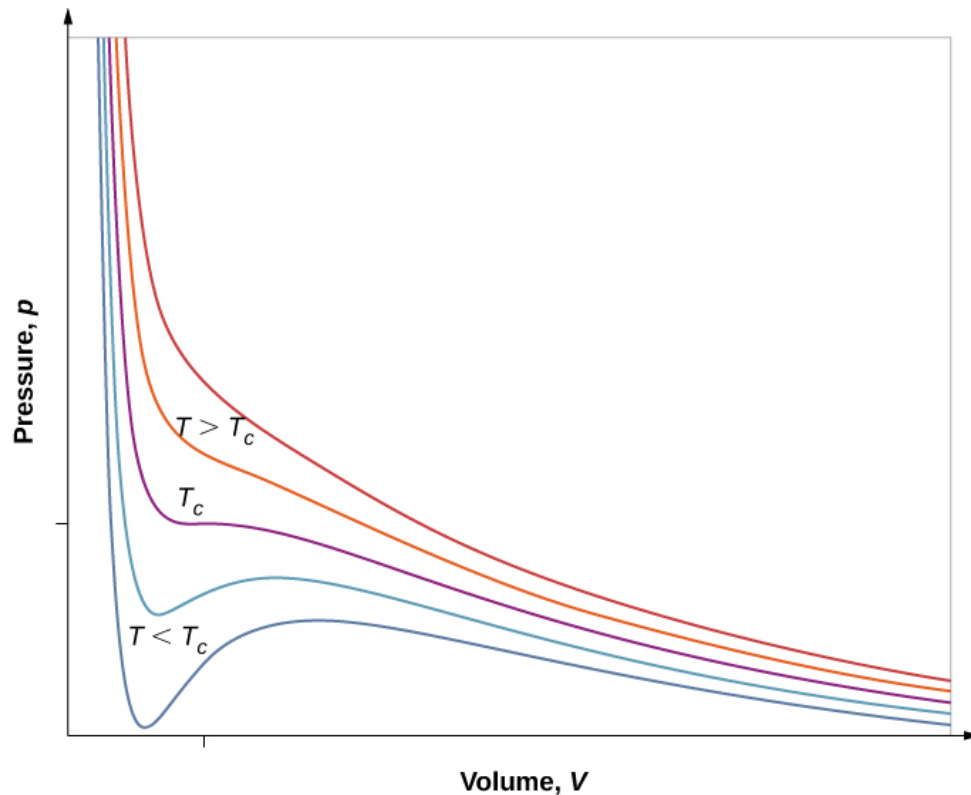
In the limit of low density (small n), the a and b terms are negligible, and we have the ideal gas law, as we should for low density. On the other hand, if $V - nb$ is small, meaning that the molecules are very close together, the pressure must be higher to give the same nRT , as we would expect in the situation of a highly compressed gas. However, the increase in pressure is less than that argument would suggest, because at high density the $(n/V)^2$ term is significant. Since it's positive, it causes a lower pressure to give the same nRT .

The van der Waals equation of state works well for most gases under a wide variety of conditions. As we'll see in the next module, it even predicts the gas-liquid transition.

pV Diagrams

We can examine aspects of the behavior of a substance by plotting a **pV diagram**, which is a graph of pressure versus volume. When the substance behaves like an ideal gas, the ideal gas law $pV = nRT$ describes the relationship between its pressure and volume. On a pV diagram, it's common to plot an *isotherm*, which is a curve showing p as a function of V with the number of molecules and the temperature fixed. Then, for an ideal gas, $pV = \text{constant}$. For example, the volume of the gas decreases as the pressure increases. The resulting graph is a hyperbola.

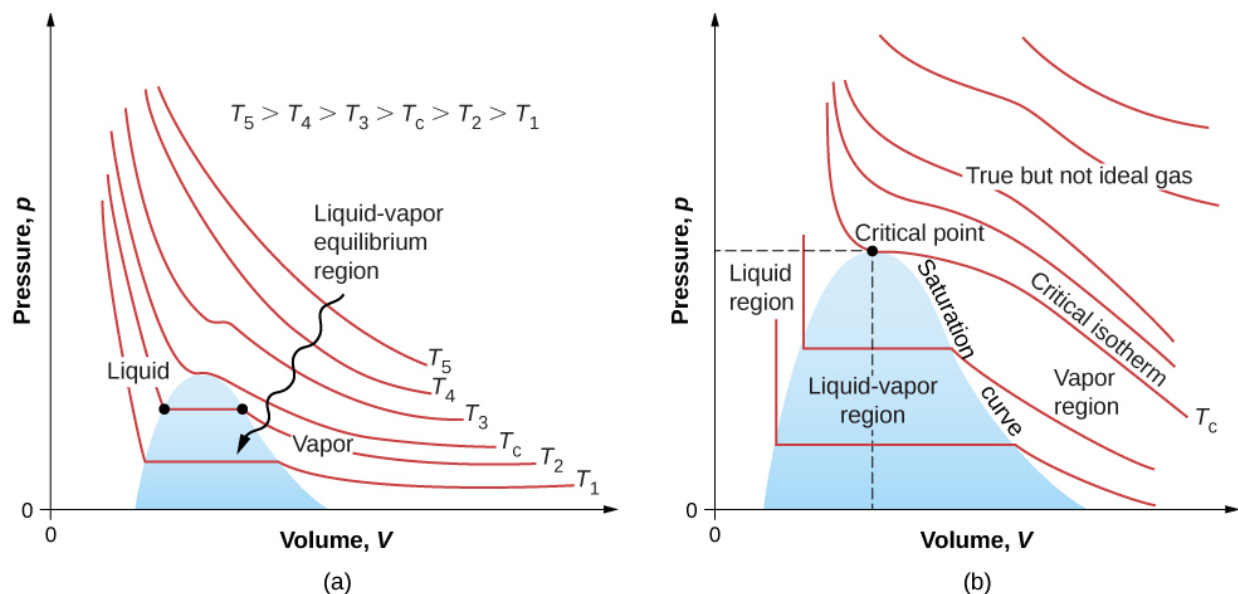
However, if we assume the van der Waals equation of state, the isotherms become more interesting, as shown in [\[link\]](#). At high temperatures, the curves are approximately hyperbolas, representing approximately ideal behavior at various fixed temperatures. At lower temperatures, the curves look less and less like hyperbolas—that is, the gas is not behaving ideally. There is a **critical temperature** T_c at which the curve has a point with zero slope. Below that temperature, the curves do not decrease monotonically; instead, they each have a “hump,” meaning that for a certain range of volume, increasing the volume increases the pressure.



pV diagram for a Van der Waals gas at various temperatures. The red curves are calculated at temperatures above the critical temperature and the blue curves at temperatures below it. The blue curves have an oscillation in which volume (V) increases with increasing temperature (T), an impossible situation, so they must be corrected as in [\[link\]](#). (credit: “Eman”/Wikimedia Commons)

Such behavior would be completely unphysical. Instead, the curves are understood as describing a liquid-gas phase transition. The oscillating part of the curve is replaced by a horizontal line, showing that as the volume increases at constant temperature, the pressure stays constant. That behavior corresponds to boiling and condensation; when a substance is at its boiling temperature for a particular pressure, it can increase in volume as some of the liquid turns to gas, or decrease as some of the gas turns to liquid, without any change in temperature or pressure.

[\[link\]](#) shows similar isotherms that are more realistic than those based on the van der Waals equation. The steep parts of the curves to the left of the transition region show the liquid phase, which is almost incompressible—a slight decrease in volume requires a large increase in pressure. The flat parts show the liquid-gas transition; the blue regions that they define represent combinations of pressure and volume where liquid and gas can coexist.



pV diagrams. (a) Each curve (isotherm) represents the relationship between p and V at a fixed temperature; the upper curves are at higher temperatures. The lower curves are not hyperbolas because the gas is no longer an ideal gas. (b) An expanded portion of the pV diagram for low temperatures, where the phase can change from a gas to a liquid. The term “vapor” refers to the gas phase when it exists at a temperature below the boiling temperature.

The isotherms above T_c do not go through the liquid-gas transition. Therefore, liquid cannot exist above that temperature, which is the critical temperature (described in the chapter on temperature and heat). At sufficiently low pressure above that temperature, the gas has the density of a liquid but will not condense; the gas is said to be **supercritical**. At higher pressure, it is solid. Carbon dioxide, for example, has no liquid phase at a temperature above 31.0°C . The critical pressure is the maximum pressure at which the liquid can exist. The point on the pV diagram at the critical pressure and temperature is the critical point (which you learned about in the chapter on temperature and heat). [\[link\]](#) lists representative critical temperatures and pressures.

Substance	Critical temperature		Critical pressure	
	K	$^\circ\text{C}$	Pa	atm
Water	647.4	374.3	22.12×10^6	219.0
Sulfur dioxide	430.7	157.6	7.88×10^6	78.0
Ammonia	405.5	132.4	11.28×10^6	111.7
Carbon dioxide	304.2	31.1	7.39×10^6	73.2

Substance	Critical temperature		Critical pressure	
Oxygen	154.8	−118.4	5.08×10^6	50.3
Nitrogen	126.2	−146.9	3.39×10^6	33.6
Hydrogen	33.3	−239.9	1.30×10^6	12.9
Helium	5.3	−267.9	0.229×10^6	2.27

Critical Temperatures and Pressures for Various Substances

Summary

- The ideal gas law relates the pressure and volume of a gas to the number of gas molecules and the temperature of the gas.
- A mole of any substance has a number of molecules equal to the number of atoms in a 12-g sample of carbon-12. The number of molecules in a mole is called Avogadro's number N_A ,

Equation:

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}.$$

- A mole of any substance has a mass in grams numerically equal to its molecular mass in unified mass units, which can be determined from the periodic table of elements. The ideal gas law can also be written and solved in terms of the number of moles of gas:

Equation:

$$pV = nRT,$$

where n is the number of moles and R is the universal gas constant,

Equation:

$$R = 8.31 \text{ J/mol} \cdot \text{K}.$$

- The ideal gas law is generally valid at temperatures well above the boiling temperature.
- The van der Waals equation of state for gases is valid closer to the boiling point than the ideal gas law.
- Above the critical temperature and pressure for a given substance, the liquid phase does not exist, and the sample is “supercritical.”

Conceptual Questions

Exercise:

Problem:

Two H_2 molecules can react with one O_2 molecule to produce two H_2O molecules. How many moles of hydrogen molecules are needed to react with one mole of oxygen molecules?

Solution:

2 moles, as that will contain twice as many molecules as the 1 mole of oxygen

Exercise:**Problem:**

Under what circumstances would you expect a gas to behave significantly differently than predicted by the ideal gas law?

Exercise:**Problem:**

A constant-volume gas thermometer contains a fixed amount of gas. What property of the gas is measured to indicate its temperature?

Solution:

pressure

Exercise:**Problem:**

Inflate a balloon at room temperature. Leave the inflated balloon in the refrigerator overnight. What happens to the balloon, and why?

Exercise:**Problem:**

In the last chapter, free convection was explained as the result of buoyant forces on hot fluids. Explain the upward motion of air in flames based on the ideal gas law.

Solution:

The flame contains hot gas (heated by combustion). The pressure is still atmospheric pressure, in mechanical equilibrium with the air around it (or roughly so). The density of the hot gas is proportional to its number density N/V (neglecting the difference in composition between the gas in the flame and the surrounding air). At higher temperature than the surrounding air, the ideal gas law says that $N/V = p/k_B T$ is less than that of the surrounding air. Therefore the hot air has lower density than the surrounding air and is lifted by the buoyant force.

Problems**Exercise:****Problem:**

The gauge pressure in your car tires is $2.50 \times 10^5 \text{ N/m}^2$ at a temperature of 35.0°C when you drive it onto a ship in Los Angeles to be sent to Alaska. What is their gauge pressure on a night in Alaska when their temperature has dropped to -40.0°C ? Assume the tires have not gained or lost any air.

Exercise:

Problem:

Suppose a gas-filled incandescent light bulb is manufactured so that the gas inside the bulb is at atmospheric pressure when the bulb has a temperature of $20.0\text{ }^{\circ}\text{C}$. (a) Find the gauge pressure inside such a bulb when it is hot, assuming its average temperature is $60.0\text{ }^{\circ}\text{C}$ (an approximation) and neglecting any change in volume due to thermal expansion or gas leaks. (b) The actual final pressure for the light bulb will be less than calculated in part (a) because the glass bulb will expand. Is this effect significant?

Solution:

a. 0.137 atm ; b. $p_g = (1\text{ atm})\frac{T_2V_1}{T_1V_2} - 1\text{ atm}$. Because of the expansion of the glass, $V_2 = 0.99973$. Multiplying by that factor does not make any significant difference.

Exercise:**Problem:**

People buying food in sealed bags at high elevations often notice that the bags are puffed up because the air inside has expanded. A bag of pretzels was packed at a pressure of 1.00 atm and a temperature of $22.0\text{ }^{\circ}\text{C}$. When opened at a summer picnic in Santa Fe, New Mexico, at a temperature of $32.0\text{ }^{\circ}\text{C}$, the volume of the air in the bag is 1.38 times its original volume. What is the pressure of the air?

Exercise:**Problem:**

How many moles are there in (a) 0.0500 g of N_2 gas ($M = 28.0\text{ g/mol}$)? (b) 10.0 g of CO_2 gas ($M = 44.0\text{ g/mol}$)? (c) How many molecules are present in each case?

Solution:

a. $1.79 \times 10^{-3}\text{ mol}$; b. 0.227 mol ; c. 1.08×10^{21} molecules for the nitrogen, 1.37×10^{23} molecules for the carbon dioxide

Exercise:**Problem:**

A cubic container of volume 2.00 L holds 0.500 mol of nitrogen gas at a temperature of $25.0\text{ }^{\circ}\text{C}$. What is the net force due to the nitrogen on one wall of the container? Compare that force to the sample's weight.

Exercise:**Problem:**

Calculate the number of moles in the 2.00-L volume of air in the lungs of the average person. Note that the air is at $37.0\text{ }^{\circ}\text{C}$ (body temperature) and that the total volume in the lungs is several times the amount inhaled in a typical breath as given in [\[link\]](#).

Solution:

$7.84 \times 10^{-2}\text{ mol}$

Exercise:

Problem:

An airplane passenger has 100 cm^3 of air in his stomach just before the plane takes off from a sea-level airport. What volume will the air have at cruising altitude if cabin pressure drops to $7.50 \times 10^4 \text{ N/m}^2$?

Exercise:**Problem:**

A company advertises that it delivers helium at a gauge pressure of $1.72 \times 10^7 \text{ Pa}$ in a cylinder of volume 43.8 L. How many balloons can be inflated to a volume of 4.00 L with that amount of helium? Assume the pressure inside the balloons is $1.01 \times 10^5 \text{ Pa}$ and the temperature in the cylinder and the balloons is 25.0°C .

Solution:

$$1.87 \times 10^3$$

Exercise:**Problem:**

According to <http://hyperphysics.phy-astr.gsu.edu/hbase/solar/venusenv.html>, the atmosphere of Venus is approximately 96.5% CO_2 and 3.5% N_2 by volume. On the surface, where the temperature is about 750 K and the pressure is about 90 atm, what is the density of the atmosphere?

Exercise:**Problem:**

An expensive vacuum system can achieve a pressure as low as $1.00 \times 10^{-7} \text{ N/m}^2$ at 20.0°C . How many molecules are there in a cubic centimeter at this pressure and temperature?

Solution:

$$2.47 \times 10^7 \text{ molecules}$$

Exercise:**Problem:**

The number density N/V of gas molecules at a certain location in the space above our planet is about $1.00 \times 10^{11} \text{ m}^{-3}$, and the pressure is $2.75 \times 10^{-10} \text{ N/m}^2$ in this space. What is the temperature there?

Exercise:**Problem:**

A bicycle tire contains 2.00 L of gas at an absolute pressure of $7.00 \times 10^5 \text{ N/m}^2$ and a temperature of 18.0°C . What will its pressure be if you let out an amount of air that has a volume of 100 cm^3 at atmospheric pressure? Assume tire temperature and volume remain constant.

Solution:

$$6.95 \times 10^5 \text{ Pa}; 6.86 \text{ atm}$$

Exercise:**Problem:**

In a common demonstration, a bottle is heated and stoppered with a hard-boiled egg that's a little bigger than the bottle's neck. When the bottle is cooled, the pressure difference between inside and outside forces the egg into the bottle. Suppose the bottle has a volume of 0.500 L and the temperature inside it is raised to 80.0 °C while the pressure remains constant at 1.00 atm because the bottle is open. (a) How many moles of air are inside? (b) Now the egg is put in place, sealing the bottle. What is the gauge pressure inside after the air cools back to the ambient temperature of 25 °C but before the egg is forced into the bottle?

Exercise:**Problem:**

A high-pressure gas cylinder contains 50.0 L of toxic gas at a pressure of $1.40 \times 10^7 \text{ N/m}^2$ and a temperature of 25.0 °C. The cylinder is cooled to dry ice temperature (-78.5 °C) to reduce the leak rate and pressure so that it can be safely repaired. (a) What is the final pressure in the tank, assuming a negligible amount of gas leaks while being cooled and that there is no phase change? (b) What is the final pressure if one-tenth of the gas escapes? (c) To what temperature must the tank be cooled to reduce the pressure to 1.00 atm (assuming the gas does not change phase and that there is no leakage during cooling)? (d) Does cooling the tank as in part (c) appear to be a practical solution?

Solution:

a. $9.14 \times 10^6 \text{ Pa}$; b. $8.22 \times 10^6 \text{ Pa}$; c. 2.15 K; d. no

Exercise:**Problem:**

Find the number of moles in 2.00 L of gas at 35.0 °C and under $7.41 \times 10^7 \text{ N/m}^2$ of pressure.

Exercise:**Problem:**

Calculate the depth to which Avogadro's number of table tennis balls would cover Earth. Each ball has a diameter of 3.75 cm. Assume the space between balls adds an extra 25.0% to their volume and assume they are not crushed by their own weight.

Solution:

40.7 km

Exercise:**Problem:**

(a) What is the gauge pressure in a 25.0 °C car tire containing 3.60 mol of gas in a 30.0-L volume? (b) What will its gauge pressure be if you add 1.00 L of gas originally at atmospheric pressure and 25.0 °C? Assume the temperature remains at 25.0 °C and the volume remains constant.

Glossary

Avogadro's number

N_A , the number of molecules in one mole of a substance; $N_A = 6.02 \times 10^{23}$ particles/mole

Boltzmann constant

k_B , a physical constant that relates energy to temperature and appears in the ideal gas law;

$$k_B = 1.38 \times 10^{-23} \text{ J/K}$$

critical temperature

T_c at which the isotherm has a point with zero slope

ideal gas

gas at the limit of low density and high temperature

ideal gas law

physical law that relates the pressure and volume of a gas, far from liquefaction, to the number of gas molecules or number of moles of gas and the temperature of the gas

mole

quantity of a substance whose mass (in grams) is equal to its molecular mass

pV diagram

graph of pressure vs. volume

supercritical

condition of a fluid being at such a high temperature and pressure that the liquid phase cannot exist

universal gas constant

R , the constant that appears in the ideal gas law expressed in terms of moles, given by $R = N_A k_B$

van der Waals equation of state

equation, typically approximate, which relates the pressure and volume of a gas to the number of gas molecules or number of moles of gas and the temperature of the gas

Pressure, Temperature, and RMS Speed

By the end of this section, you will be able to:

- Explain the relations between microscopic and macroscopic quantities in a gas
- Solve problems involving mixtures of gases
- Solve problems involving the distance and time between a gas molecule's collisions

We have examined pressure and temperature based on their macroscopic definitions. Pressure is the force divided by the area on which the force is exerted, and temperature is measured with a thermometer. We can gain a better understanding of pressure and temperature from the **kinetic theory of gases**, the theory that relates the macroscopic properties of gases to the motion of the molecules they consist of. First, we make two assumptions about molecules in an ideal gas.

1. There is a very large number N of molecules, all identical and each having mass m .
2. The molecules obey Newton's laws and are in continuous motion, which is random and isotropic, that is, the same in all directions.

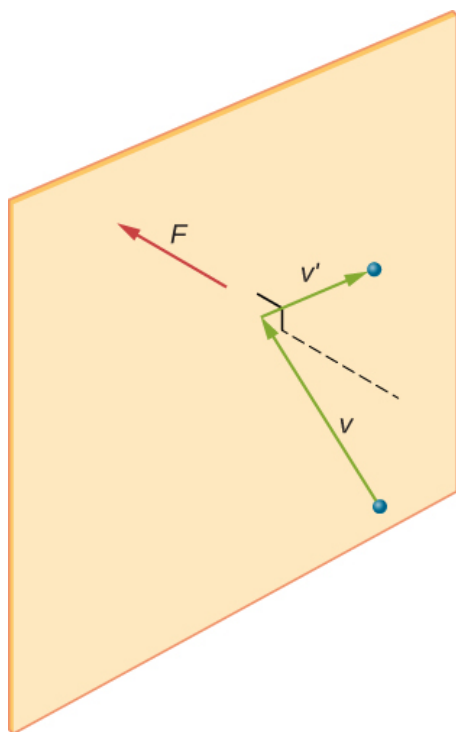
To derive the ideal gas law and the connection between microscopic quantities such as the energy of a typical molecule and macroscopic quantities such as temperature, we analyze a sample of an ideal gas in a rigid container, about which we make two further assumptions:

3. The molecules are much smaller than the average distance between them, so their total volume is much less than that of their container (which has volume V). In other words, we take the Van der Waals constant b , the volume of a mole of gas molecules, to be negligible compared to the volume of a mole of gas in the container.
4. The molecules make perfectly elastic collisions with the walls of the container and with each other. Other forces on them, including gravity and the attractions represented by the Van der Waals constant a , are negligible (as is necessary for the assumption of isotropy).

The collisions between molecules do not appear in the derivation of the ideal gas law. They do not disturb the derivation either, since collisions between molecules moving with random velocities give new random velocities. Furthermore, if the velocities of gas molecules in a container are initially not random and isotropic, molecular collisions are what make them random and isotropic.

We make still further assumptions that simplify the calculations but do not affect the result. First, we let the container be a rectangular box. Second, we begin by considering *monatomic* gases, those whose molecules consist of single atoms, such as helium. Then, we can assume that the atoms have no energy except their translational kinetic energy; for instance, they have neither rotational nor vibrational energy. (Later, we discuss the validity of this assumption for real monatomic gases and dispense with it to consider diatomic and polyatomic gases.)

[\[link\]](#) shows a collision of a gas molecule with the wall of a container, so that it exerts a force on the wall (by Newton's third law). These collisions are the source of pressure in a gas. As the number of molecules increases, the number of collisions, and thus the pressure, increases. Similarly, if the average velocity of the molecules is higher, the gas pressure is higher.



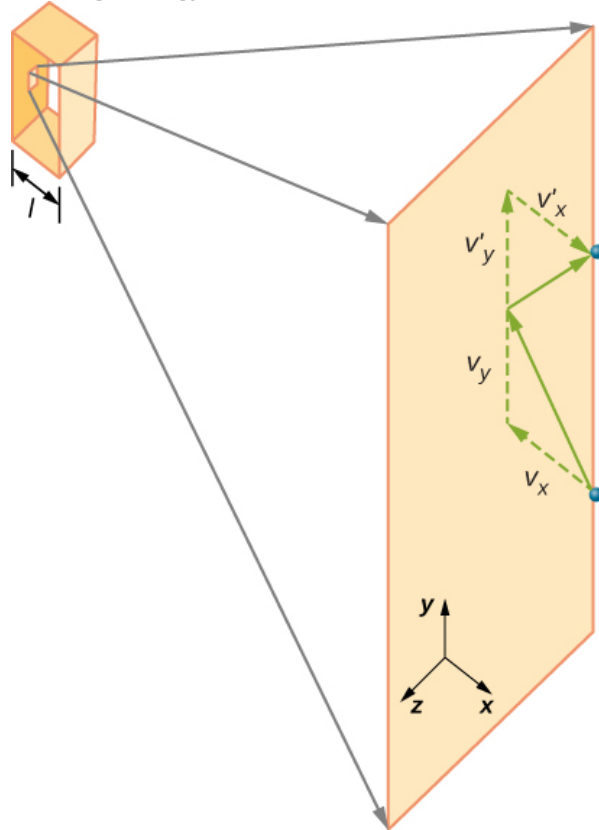
When a molecule collides with a rigid wall, the component of its momentum perpendicular to the wall is reversed. A force is thus exerted on the wall, creating pressure.

In a sample of gas in a container, the randomness of the molecular motion causes the number of collisions of molecules with any part of the wall in a given time to fluctuate. However, because a huge number of molecules collide with the wall in a short time, the number of collisions on the scales of time and space we measure fluctuates by only a tiny, usually unobservable fraction from the average. We can compare this situation to that of a casino, where the outcomes of the bets are random and the casino's takings fluctuate by the minute and the hour. However, over long times such as a year, the casino's takings are very close to the averages expected from the odds. A tank of gas has enormously more molecules than a casino has bettors in a year, and the molecules make enormously more collisions in a second than a casino has bets.

A calculation of the average force exerted by molecules on the walls of the box leads us to the ideal gas law and to the connection between temperature and molecular kinetic energy. (In fact, we will take two averages: one over time to get the average force exerted by one molecule with a given velocity, and then another average over molecules with different velocities.) This approach was developed by Daniel Bernoulli (1700–1782), who is best known in physics for his work on fluid flow (hydrodynamics). Remarkably, Bernoulli did this work before Dalton established the view of matter as consisting of atoms.

[\[link\]](#) shows a container full of gas and an expanded view of an elastic collision of a gas molecule with a wall of the container, broken down into components. We have assumed that a molecule is small compared with the separation of molecules in the gas, and that its interaction with other molecules can be ignored.

Under these conditions, the ideal gas law is experimentally valid. Because we have also assumed the wall is rigid and the particles are points, the collision is elastic (by conservation of energy—there's nowhere for a particle's kinetic energy to go). Therefore, the molecule's kinetic energy remains constant, and hence, its speed and the magnitude of its momentum remain constant as well. This assumption is not always valid, but the results in the rest of this module are also obtained in models that let the molecules exchange energy and momentum with the wall.



Gas in a box exerts an outward pressure on its walls. A molecule colliding with a rigid wall has its velocity and momentum in the x -direction reversed. This direction is perpendicular to the wall. The components of its velocity momentum in the y - and z -directions are not changed, which means there is no force parallel to the wall.

If the molecule's velocity changes in the x -direction, its momentum changes from $-mv_x$ to $+mv_x$. Thus, its change in momentum is $\Delta mv = +mv_x - (-mv_x) = 2mv_x$. According to the impulse-momentum theorem given in the chapter on linear momentum and collisions, the force exerted on the i th molecule, where i labels the molecules from 1 to N , is given by

Equation:

$$F_i = \frac{\Delta p_i}{\Delta t} = \frac{2mv_{ix}}{\Delta t}.$$

(In this equation alone, p represents momentum, not pressure.) There is no force between the wall and the molecule except while the molecule is touching the wall. During the short time of the collision, the force between the molecule and wall is relatively large, but that is not the force we are looking for. We are looking for the average force, so we take Δt to be the average time between collisions of the given molecule with this wall, which is the time in which we expect to find one collision. Let l represent the length of the box in the x -direction. Then Δt is the time the molecule would take to go across the box and back, a distance $2l$, at a speed of v_x . Thus $\Delta t = 2l/v_x$, and the expression for the force becomes

Equation:

$$F_i = \frac{2mv_{ix}}{2l/v_{ix}} = \frac{mv_{ix}^2}{l}.$$

This force is due to *one* molecule. To find the total force on the wall, F , we need to add the contributions of all N molecules:

Equation:

$$F = \sum_{i=1}^N F_i = \sum_{i=1}^N \frac{mv_{ix}^2}{l} = \frac{m}{l} \sum_{i=1}^N v_{ix}^2.$$

We now use the definition of the average, which we denote with a bar, to find the force:

Equation:

$$F = N \frac{m}{l} \left(\frac{1}{N} \sum_{i=1}^N v_{ix}^2 \right) = N \frac{m \bar{v_x^2}}{l}.$$

We want the force in terms of the speed v , rather than the x -component of the velocity. Note that the total velocity squared is the sum of the squares of its components, so that

Equation:

$$\bar{v^2} = \bar{v_x^2} + \bar{v_y^2} + \bar{v_z^2}.$$

With the assumption of isotropy, the three averages on the right side are equal, so

Equation:

$$\bar{v^2} = 3\bar{v_{ix}^2}.$$

Substituting this into the expression for F gives

Equation:

$$F = N \frac{m \bar{v^2}}{3l}.$$

The pressure is F/A , so we obtain

Equation:

$$p = \frac{F}{A} = N \frac{m\bar{v}^2}{3Al} = \frac{Nm\bar{v}^2}{3V},$$

where we used $V = Al$ for the volume. This gives the important result

Note:

Equation:

$$pV = \frac{1}{3} Nm\bar{v}^2.$$

Combining this equation with $pV = Nk_{\text{B}}T$ gives

Equation:

$$\frac{1}{3} Nm\bar{v}^2 = Nk_{\text{B}}T.$$

We can get the average kinetic energy of a molecule, $\frac{1}{2} m\bar{v}^2$, from the left-hand side of the equation by dividing out N and multiplying by $3/2$.

Note:

Average Kinetic Energy per Molecule

The average kinetic energy of a molecule is directly proportional to its absolute temperature:

Equation:

$$\bar{K} = \frac{1}{2} m\bar{v}^2 = \frac{3}{2} k_{\text{B}}T.$$

The equation $\bar{K} = \frac{3}{2} k_{\text{B}}T$ is the average kinetic energy per molecule. Note in particular that nothing in this equation depends on the molecular mass (or any other property) of the gas, the pressure, or anything but the temperature. If samples of helium and xenon gas, with very different molecular masses, are at the same temperature, the molecules have the same average kinetic energy.

The **internal energy** of a thermodynamic system is the sum of the mechanical energies of all of the molecules in it. We can now give an equation for the internal energy of a monatomic ideal gas. In such a gas, the molecules' only energy is their translational kinetic energy. Therefore, denoting the internal energy by E_{int} , we simply have $E_{\text{int}} = N\bar{K}$, or

Note:

Equation:

$$E_{\text{int}} = \frac{3}{2} N k_{\text{B}} T.$$

Often we would like to use this equation in terms of moles:

Equation:

$$E_{\text{int}} = \frac{3}{2} n R T.$$

We can solve $\bar{K} = \frac{1}{2} m \bar{v}^2 = \frac{3}{2} k_{\text{B}} T$ for a typical speed of a molecule in an ideal gas in terms of temperature to determine what is known as the *root-mean-square (rms) speed* of a molecule.

Note:

RMS Speed of a Molecule

The **root-mean-square (rms) speed** of a molecule, or the square root of the average of the square of the speed \bar{v}^2 , is

Equation:

$$v_{\text{rms}} = \sqrt{\bar{v}^2} = \sqrt{\frac{3 k_{\text{B}} T}{m}}.$$

The rms speed is not the average or the most likely speed of molecules, as we will see in [Distribution of Molecular Speeds](#), but it provides an easily calculated estimate of the molecules' speed that is related to their kinetic energy. Again we can write this equation in terms of the gas constant R and the molar mass M in kg/mol:

Note:

Equation:

$$v_{\text{rms}} = \sqrt{\frac{3 R T}{M}}.$$

We digress for a moment to answer a question that may have occurred to you: When we apply the model to atoms instead of theoretical point particles, does rotational kinetic energy change our results? To answer this question, we have to appeal to quantum mechanics. In quantum mechanics, rotational kinetic energy cannot take on just any value; it's limited to a discrete set of values, and the smallest value is inversely proportional to the rotational inertia. The rotational inertia of an atom is tiny because almost all

of its mass is in the nucleus, which typically has a radius less than 10^{-14} m. Thus the minimum rotational energy of an atom is much more than $\frac{1}{2} k_B T$ for any attainable temperature, and the energy available is not enough to make an atom rotate. We will return to this point when discussing diatomic and polyatomic gases in the next section.

Example:

Calculating Kinetic Energy and Speed of a Gas Molecule

(a) What is the average kinetic energy of a gas molecule at 20.0°C (room temperature)? (b) Find the rms speed of a nitrogen molecule (N_2) at this temperature.

Strategy

(a) The known in the equation for the average kinetic energy is the temperature:

Equation:

$$\bar{K} = \frac{1}{2} m \bar{v}^2 = \frac{3}{2} k_B T.$$

Before substituting values into this equation, we must convert the given temperature into kelvin:

$T = (20.0 + 273) \text{ K} = 293 \text{ K}$. We can find the rms speed of a nitrogen molecule by using the equation

Equation:

$$v_{\text{rms}} = \sqrt{\bar{v}^2} = \sqrt{\frac{3k_B T}{m}},$$

but we must first find the mass of a nitrogen molecule. Obtaining the molar mass of nitrogen N_2 from the periodic table, we find

Equation:

$$m = \frac{M}{N_A} = \frac{2 (14.0067) \times 10^{-3} \text{ kg/mol}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 4.65 \times 10^{-26} \text{ kg}.$$

Solution

- a. The temperature alone is sufficient for us to find the average translational kinetic energy. Substituting the temperature into the translational kinetic energy equation gives

Equation:

$$\bar{K} = \frac{3}{2} k_B T = \frac{3}{2} (1.38 \times 10^{-23} \text{ J/K})(293 \text{ K}) = 6.07 \times 10^{-21} \text{ J}.$$

- b. Substituting this mass and the value for k_B into the equation for v_{rms} yields

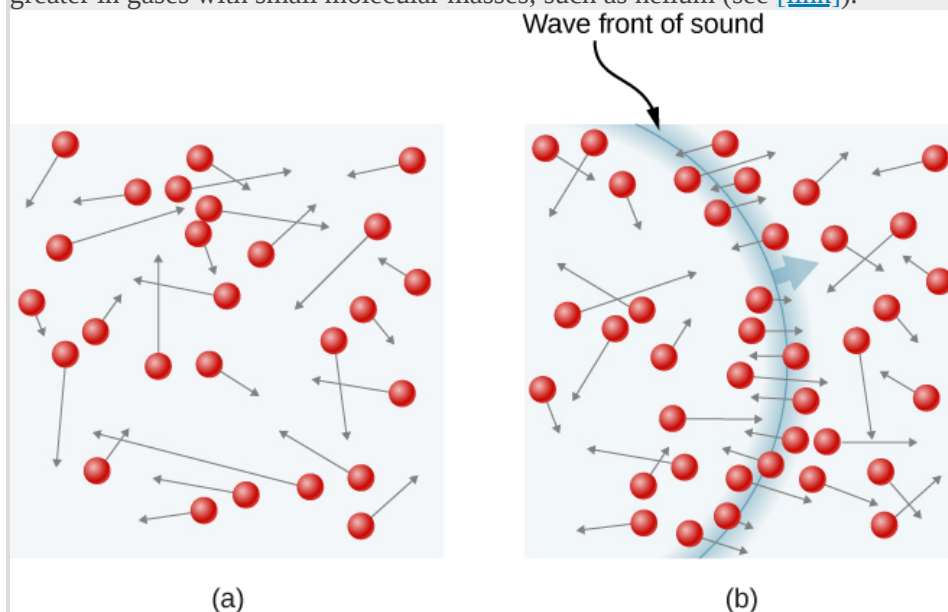
Equation:

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})}{4.65 \times 10^{-26} \text{ kg}}} = 511 \text{ m/s}.$$

Significance

Note that the average kinetic energy of the molecule is independent of the type of molecule. The average translational kinetic energy depends only on absolute temperature. The kinetic energy is very small compared to macroscopic energies, so that we do not feel when an air molecule is hitting our skin. On the

other hand, it is much greater than the typical difference in gravitational potential energy when a molecule moves from, say, the top to the bottom of a room, so our neglect of gravitation is justified in typical real-world situations. The rms speed of the nitrogen molecule is surprisingly large. These large molecular velocities do not yield macroscopic movement of air, since the molecules move in all directions with equal likelihood. The *mean free path* (the distance a molecule moves on average between collisions, discussed a bit later in this section) of molecules in air is very small, so the molecules move rapidly but do not get very far in a second. The high value for rms speed is reflected in the speed of sound, which is about 340 m/s at room temperature. The higher the rms speed of air molecules, the faster sound vibrations can be transferred through the air. The speed of sound increases with temperature and is greater in gases with small molecular masses, such as helium (see [\[link\]](#)).



(a) In an ordinary gas, so many molecules move so fast that they collide billions of times every second. (b) Individual molecules do not move very far in a small amount of time, but disturbances like sound waves are transmitted at speeds related to the molecular speeds.

Example:

Calculating Temperature: Escape Velocity of Helium Atoms

To escape Earth's gravity, an object near the top of the atmosphere (at an altitude of 100 km) must travel away from Earth at 11.1 km/s. This speed is called the *escape velocity*. At what temperature would helium atoms have an rms speed equal to the escape velocity?

Strategy

Identify the knowns and unknowns and determine which equations to use to solve the problem.

Solution

1. Identify the knowns: v is the escape velocity, 11.1 km/s.
2. Identify the unknowns: We need to solve for temperature, T . We also need to solve for the mass m of the helium atom.
3. Determine which equations are needed.

- To get the mass m of the helium atom, we can use information from the periodic table:

Equation:

$$m = \frac{M}{N_A}.$$

- To solve for temperature T , we can rearrange

Equation:

$$\frac{1}{2} m \bar{v}^2 = \frac{3}{2} k_B T$$

to yield

Equation:

$$T = \frac{m \bar{v}^2}{3 k_B}.$$

4. Substitute the known values into the equations and solve for the unknowns,

Equation:

$$m = \frac{M}{N_A} = \frac{4.0026 \times 10^{-3} \text{ kg/mol}}{6.02 \times 10^{23} \text{ mol}} = 6.65 \times 10^{-27} \text{ kg}$$

and

Equation:

$$T = \frac{(6.65 \times 10^{-27} \text{ kg}) (11.1 \times 10^3 \text{ m/s})^2}{3 (1.38 \times 10^{-23} \text{ J/K})} = 1.98 \times 10^4 \text{ K}.$$

Significance

This temperature is much higher than atmospheric temperature, which is approximately 250 K (-25°C or -10°F) at high elevation. Very few helium atoms are left in the atmosphere, but many were present when the atmosphere was formed, and more are always being created by radioactive decay (see the chapter on nuclear physics). The reason for the loss of helium atoms is that a small number of helium atoms have speeds higher than Earth's escape velocity even at normal temperatures. The speed of a helium atom changes from one collision to the next, so that at any instant, there is a small but nonzero chance that the atom's speed is greater than the escape velocity. The chance is high enough that over the lifetime of Earth, almost all the helium atoms that have been in the atmosphere have reached escape velocity at high altitudes and escaped from Earth's gravitational pull. Heavier molecules, such as oxygen, nitrogen, and water, have smaller rms speeds, and so it is much less likely that any of them will have speeds greater than the escape velocity. In fact, the likelihood is so small that billions of years are required to lose significant amounts of heavier molecules from the atmosphere. [\[link\]](#) shows the effect of a lack of an atmosphere on the Moon. Because the gravitational pull of the Moon is much weaker, it has lost almost its entire atmosphere. The atmospheres of Earth and other bodies are compared in this chapter's exercises.



This photograph of Apollo 17 Commander Eugene Cernan driving the lunar rover on the Moon in 1972 looks as though it was taken at night with a large spotlight. In fact, the light is coming from the Sun. Because the acceleration due to gravity on the Moon is so low (about $1/6$ that of Earth), the Moon's escape velocity is much smaller. As a result, gas molecules escape very easily from the Moon, leaving it with virtually no atmosphere. Even during the daytime, the sky is black because there is no gas to scatter sunlight.
(credit: Harrison H. Schmitt/NASA)

Note:

Exercise:

Problem:

Check Your Understanding If you consider a very small object, such as a grain of pollen, in a gas, then the number of molecules striking its surface would also be relatively small. Would you expect the grain of pollen to experience any fluctuations in pressure due to statistical fluctuations in the number of gas molecules striking it in a given amount of time?

Solution:

Yes. Such fluctuations actually occur for a body of any size in a gas, but since the numbers of molecules are immense for macroscopic bodies, the fluctuations are a tiny percentage of the number

of collisions, and the averages spoken of in this section vary imperceptibly. Roughly speaking, the fluctuations are inversely proportional to the square root of the number of collisions, so for small bodies, they can become significant. This was actually observed in the nineteenth century for pollen grains in water and is known as Brownian motion.

Vapor Pressure, Partial Pressure, and Dalton's Law

The pressure a gas would create if it occupied the total volume available is called the gas's **partial pressure**. If two or more gases are mixed, they will come to thermal equilibrium as a result of collisions between molecules; the process is analogous to heat conduction as described in the chapter on temperature and heat. As we have seen from kinetic theory, when the gases have the same temperature, their molecules have the same average kinetic energy. Thus, each gas obeys the ideal gas law separately and exerts the same pressure on the walls of a container that it would if it were alone. Therefore, in a mixture of gases, *the total pressure is the sum of partial pressures of the component gases*, assuming ideal gas behavior and no chemical reactions between the components. This law is known as **Dalton's law of partial pressures**, after the English scientist John Dalton (1766–1844) who proposed it. Dalton's law is consistent with the fact that pressures add according to Pascal's principle.

In a mixture of ideal gases in thermal equilibrium, the number of molecules of each gas is proportional to its partial pressure. This result follows from applying the ideal gas law to each in the form $p/n = RT/V$. Because the right-hand side is the same for any gas at a given temperature in a container of a given volume, the left-hand side is the same as well.

- Partial pressure is the pressure a gas would create if it existed alone.
- Dalton's law states that the total pressure is the sum of the partial pressures of all of the gases present.
- For any two gases (labeled 1 and 2) in equilibrium in a container, $\frac{p_1}{n_1} = \frac{p_2}{n_2}$.

An important application of partial pressure is that, in chemistry, it functions as the concentration of a gas in determining the rate of a reaction. Here, we mention only that the partial pressure of oxygen in a person's lungs is crucial to life and health. Breathing air that has a partial pressure of oxygen below 0.16 atm can impair coordination and judgment, particularly in people not acclimated to a high elevation. Lower partial pressures of O_2 have more serious effects; partial pressures below 0.06 atm can be quickly fatal, and permanent damage is likely even if the person is rescued. However, the sensation of needing to breathe, as when holding one's breath, is caused much more by high concentrations of carbon dioxide in the blood than by low concentrations of oxygen. Thus, if a small room or closet is filled with air having a low concentration of oxygen, perhaps because a leaking cylinder of some compressed gas is stored there, a person will not feel any "choking" sensation and may go into convulsions or lose consciousness without noticing anything wrong. Safety engineers give considerable attention to this danger.

Another important application of partial pressure is **vapor pressure**, which is the partial pressure of a vapor at which it is in equilibrium with the liquid (or solid, in the case of sublimation) phase of the same substance. At any temperature, the partial pressure of the water in the air cannot exceed the vapor pressure of the water at that temperature, because whenever the partial pressure reaches the vapor pressure, water condenses out of the air. Dew is an example of this condensation. The temperature at which condensation occurs for a sample of air is called the *dew point*. It is easily measured by slowly cooling a metal ball; the dew point is the temperature at which condensation first appears on the ball.

The vapor pressures of water at some temperatures of interest for meteorology are given in [\[link\]](#).

T (°C)	Vapor Pressure (Pa)
0	610.5
3	757.9
5	872.3
8	1073
10	1228
13	1497
15	1705
18	2063
20	2338
23	2809
25	3167
30	4243
35	5623
40	7376

Vapor Pressure of Water at Various Temperatures

The *relative humidity* (R.H.) at a temperature T is defined by

Equation:

$$\text{R.H.} = \frac{\text{Partial pressure of water vapor at } T}{\text{Vapor pressure of water at } T} \times 100\%.$$

A relative humidity of 100 % means that the partial pressure of water is equal to the vapor pressure; in other words, the air is saturated with water.

Example:

Calculating Relative Humidity

What is the relative humidity when the air temperature is 25 °C and the dew point is 15 °C?

Strategy

We simply look up the vapor pressure at the given temperature and that at the dew point and find the ratio.

Solution

Equation:

$$\text{R.H.} = \frac{\text{Partial pressure of water vapor at } 15^\circ\text{C}}{\text{Partial pressure of water vapor at } 25^\circ\text{C}} \times 100\% = \frac{1705 \text{ Pa}}{3167 \text{ Pa}} \times 100\% = 53.8\%.$$

Significance

R.H. is important to our comfort. The value of 53.8% is within the range of 40% to 60% recommended for comfort indoors.

As noted in the chapter on temperature and heat, the temperature seldom falls below the dew point, because when it reaches the dew point or frost point, water condenses and releases a relatively large amount of latent heat of vaporization.

Mean Free Path and Mean Free Time

We now consider collisions explicitly. The usual first step (which is all we'll take) is to calculate the **mean free path**, λ , the average distance a molecule travels between collisions with other molecules, and the *mean free time* τ , the average time between the collisions of a molecule. If we assume all the molecules are spheres with a radius r , then a molecule will collide with another if their centers are within a distance $2r$ of each other. For a given particle, we say that the area of a circle with that radius, $4\pi r^2$, is the "cross-section" for collisions. As the particle moves, it traces a cylinder with that cross-sectional area. The mean free path is the length λ such that the expected number of other molecules in a cylinder of length λ and cross-section $4\pi r^2$ is 1. If we temporarily ignore the motion of the molecules other than the one we're looking at, the expected number is the number density of molecules, N/V , times the volume, and the volume is $4\pi r^2\lambda$, so we have $(N/V)4\pi r^2\lambda = 1$, or

Equation:

$$\lambda = \frac{V}{4\pi r^2 N}.$$

Taking the motion of all the molecules into account makes the calculation much harder, but the only change is a factor of $\sqrt{2}$. The result is

Note:

Equation:

$$\lambda = \frac{V}{4\sqrt{2}\pi r^2 N}.$$

In an ideal gas, we can substitute $V/N = k_B T/p$ to obtain

Note:

Equation:

$$\lambda = \frac{k_B T}{4\sqrt{2}\pi r^2 p}.$$

The **mean free time** τ is simply the mean free path divided by a typical speed, and the usual choice is the rms speed. Then

Note:

Equation:

$$\tau = \frac{k_{\text{B}}T}{4\sqrt{2}\pi r^2 p v_{\text{rms}}}.$$

Example:

Calculating Mean Free Time

Find the mean free time for argon atoms ($M = 39.9 \text{ g/mol}$) at a temperature of 0°C and a pressure of 1.00 atm . Take the radius of an argon atom to be $1.70 \times 10^{-10} \text{ m}$.

Solution

1. Identify the knowns and convert into SI units. We know the molar mass is 0.0399 kg/mol , the temperature is 273 K , the pressure is $1.01 \times 10^5 \text{ Pa}$, and the radius is $1.70 \times 10^{-10} \text{ m}$.
2. Find the rms speed: $v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = 413 \frac{\text{m}}{\text{s}}$.
3. Substitute into the equation for the mean free time:

Equation:

$$\tau = \frac{k_{\text{B}}T}{4\sqrt{2}\pi r^2 p v_{\text{rms}}} = \frac{(1.38 \times 10^{-23} \text{ J/K})(273 \text{ K})}{4\sqrt{2}\pi(1.70 \times 10^{-10} \text{ m})^2(1.01 \times 10^5 \text{ Pa})(413 \text{ m/s})} = 1.76 \times 10^{-10} \text{ s}.$$

Significance

We can hardly compare this result with our intuition about gas molecules, but it gives us a picture of molecules colliding with extremely high frequency.

Note:

Exercise:

Problem:

Check Your Understanding Which has a longer mean free path, liquid water or water vapor in the air?

Solution:

In a liquid, the molecules are very close together, constantly colliding with one another. For a gas to be nearly ideal, as air is under ordinary conditions, the molecules must be very far apart. Therefore

the mean free path is much longer in the air.

Summary

- Kinetic theory is the atomic description of gases as well as liquids and solids. It models the properties of matter in terms of continuous random motion of molecules.
- The ideal gas law can be expressed in terms of the mass of the gas's molecules and $\overline{v^2}$, the average of the molecular speed squared, instead of the temperature.
- The temperature of gases is proportional to the average translational kinetic energy of molecules. Hence, the typical speed of gas molecules v_{rms} is proportional to the square root of the temperature and inversely proportional to the square root of the molecular mass.
- In a mixture of gases, each gas exerts a pressure equal to the total pressure times the fraction of the mixture that the gas makes up.
- The mean free path (the average distance between collisions) and the mean free time of gas molecules are proportional to the temperature and inversely proportional to the molar density and the molecules' cross-sectional area.

Conceptual Questions

Exercise:

Problem:

How is momentum related to the pressure exerted by a gas? Explain on the molecular level, considering the behavior of molecules.

Exercise:

Problem:

If one kind of molecule has double the radius of another and eight times the mass, how do their mean free paths under the same conditions compare? How do their mean free times compare?

Solution:

The mean free path is inversely proportional to the square of the radius, so it decreases by a factor of 4. The mean free time is proportional to the mean free path and inversely proportional to the rms speed, which in turn is inversely proportional to the square root of the mass. That gives a factor of $\sqrt{8}$ in the numerator, so the mean free time decreases by a factor of $\sqrt{2}$.

Exercise:

Problem: What is the average *velocity* of the air molecules in the room where you are right now?

Exercise:

Problem:

Why do the atmospheres of Jupiter, Saturn, Uranus, and Neptune, which are much more massive and farther from the Sun than Earth is, contain large amounts of hydrogen and helium?

Solution:

Since they're more massive, their gravity is stronger, so the escape velocity from them is higher. Since they're farther from the Sun, they're colder, so the speeds of atmospheric molecules including hydrogen and helium are lower. The combination of those facts means that relatively few hydrogen and helium molecules have escaped from the outer planets.

Exercise:

Problem:

Statistical mechanics says that in a gas maintained at a constant temperature through thermal contact with a bigger system (a "reservoir") at that temperature, the fluctuations in internal energy are typically a fraction $1/\sqrt{N}$ of the internal energy. As a fraction of the total internal energy of a mole of gas, how big are the fluctuations in the internal energy? Are we justified in ignoring them?

Exercise:

Problem:

Which is more dangerous, a closet where tanks of nitrogen are stored, or one where tanks of carbon dioxide are stored?

Solution:

One where nitrogen is stored, as excess CO_2 will cause a feeling of suffocating, but excess nitrogen and insufficient oxygen will not.

Problems

In the problems in this section, assume all gases are ideal.

Exercise:

Problem:

A person hits a tennis ball with a mass of 0.058 kg against a wall. The average component of the ball's velocity perpendicular to the wall is 11 m/s, and the ball hits the wall every 2.1 s on average, rebounding with the opposite perpendicular velocity component. (a) What is the average force exerted on the wall? (b) If the part of the wall the person hits has an area of 3.0 m^2 , what is the average pressure on that area?

Solution:

a. 0.61 N; b. 0.20 Pa

Exercise:

Problem:

A person is in a closed room (a racquetball court) with $V = 453 \text{ m}^3$ hitting a ball ($m = 42.0 \text{ g}$) around at random without any pauses. The average kinetic energy of the ball is 2.30 J. (a) What is the average value of v_x^2 ? Does it matter which direction you take to be x ? (b) Applying the methods of this chapter, find the average pressure on the walls? (c) Aside from the presence of only one "molecule" in this problem, what is the main assumption in [Pressure, Temperature, and RMS Speed](#) that does not apply here?

Exercise:

Problem:

Five bicyclists are riding at the following speeds: 5.4 m/s, 5.7 m/s, 5.8 m/s, 6.0 m/s, and 6.5 m/s. (a) What is their average speed? (b) What is their rms speed?

Solution:

a. 5.88 m/s; b. 5.89 m/s

Exercise:**Problem:**

Some incandescent light bulbs are filled with argon gas. What is v_{rms} for argon atoms near the filament, assuming their temperature is 2500 K?

Exercise:**Problem:**

Typical molecular speeds (v_{rms}) are large, even at low temperatures. What is v_{rms} for helium atoms at 5.00 K, less than one degree above helium's liquefaction temperature?

Solution:

177 m/s

Exercise:**Problem:**

What is the average kinetic energy in joules of hydrogen atoms on the 5500 °C surface of the Sun?
(b) What is the average kinetic energy of helium atoms in a region of the solar corona where the temperature is 6.00×10^5 K?

Exercise:**Problem:**

What is the ratio of the average translational kinetic energy of a nitrogen molecule at a temperature of 300 K to the gravitational potential energy of a nitrogen-molecule–Earth system at the ceiling of a 3-m-tall room with respect to the same system with the molecule at the floor?

Solution:

4.54×10^3

Exercise:**Problem:**

What is the total translational kinetic energy of the air molecules in a room of volume 23 m³ if the pressure is 9.5×10^4 Pa (the room is at fairly high elevation) and the temperature is 21 °C? Is any item of data unnecessary for the solution?

Exercise:

Problem:

The product of the pressure and volume of a sample of hydrogen gas at $0.00\text{ }^{\circ}\text{C}$ is 80.0 J . (a) How many moles of hydrogen are present? (b) What is the average translational kinetic energy of the hydrogen molecules? (c) What is the value of the product of pressure and volume at $200\text{ }^{\circ}\text{C}$?

Solution:

a. 0.0352 mol ; b. $5.65 \times 10^{-21}\text{ J}$; c. 139 J

Exercise:**Problem:**

What is the gauge pressure inside a tank of $4.86 \times 10^4\text{ mol}$ of compressed nitrogen with a volume of 6.56 m^3 if the rms speed is 514 m/s ?

Exercise:**Problem:**

If the rms speed of oxygen molecules inside a refrigerator of volume 22.0 ft^3 is 465 m/s , what is the partial pressure of the oxygen? There are 5.71 moles of oxygen in the refrigerator, and the molar mass of oxygen is 32.0 g/mol .

Solution:

21.1 kPa

Exercise:**Problem:**

The escape velocity of any object from Earth is 11.1 km/s . At what temperature would oxygen molecules (molar mass is equal to 32.0 g/mol) have root-mean-square velocity v_{rms} equal to Earth's escape velocity of 11.1 km/s ?

Exercise:**Problem:**

The escape velocity from the Moon is much smaller than that from the Earth, only 2.38 km/s . At what temperature would hydrogen molecules (molar mass is equal to 2.016 g/mol) have a root-mean-square velocity v_{rms} equal to the Moon's escape velocity?

Solution:

458 K

Exercise:**Problem:**

Nuclear fusion, the energy source of the Sun, hydrogen bombs, and fusion reactors, occurs much more readily when the average kinetic energy of the atoms is high—that is, at high temperatures. Suppose you want the atoms in your fusion experiment to have average kinetic energies of $6.40 \times 10^{-14}\text{ J}$. What temperature is needed?

Exercise:**Problem:**

Suppose that the typical speed (v_{rms}) of carbon dioxide molecules (molar mass is 44.0 g/mol) in a flame is found to be 1350 m/s. What temperature does this indicate?

Solution:

$$3.22 \times 10^3 \text{ K}$$

Exercise:**Problem:**

(a) Hydrogen molecules (molar mass is equal to 2.016 g/mol) have v_{rms} equal to 193 m/s. What is the temperature? (b) Much of the gas near the Sun is atomic hydrogen (H rather than H_2). Its temperature would have to be $1.5 \times 10^7 \text{ K}$ for the rms speed v_{rms} to equal the escape velocity from the Sun. What is that velocity?

Exercise:**Problem:**

There are two important isotopes of uranium, ^{235}U and ^{238}U ; these isotopes are nearly identical chemically but have different atomic masses. Only ^{235}U is very useful in nuclear reactors. Separating the isotopes is called uranium enrichment (and is often in the news as of this writing, because of concerns that some countries are enriching uranium with the goal of making nuclear weapons.) One of the techniques for enrichment, gas diffusion, is based on the different molecular speeds of uranium hexafluoride gas, UF_6 . (a) The molar masses of ^{235}U and $^{238}\text{UF}_6$ are 349.0 g/mol and 352.0 g/mol, respectively. What is the ratio of their typical speeds v_{rms} ? (b) At what temperature would their typical speeds differ by 1.00 m/s? (c) Do your answers in this problem imply that this technique may be difficult?

Solution:

a. 1.004; b. 764 K; c. This temperature is equivalent to 915 °F, which is high but not impossible to achieve. Thus, this process is feasible. At this temperature, however, there may be other considerations that make the process difficult. (In general, uranium enrichment by gaseous diffusion is indeed difficult and requires many passes.)

Exercise:**Problem:**

The partial pressure of carbon dioxide in the lungs is about 470 Pa when the total pressure in the lungs is 1.0 atm. What percentage of the air molecules in the lungs is carbon dioxide? Compare your result to the percentage of carbon dioxide in the atmosphere, about 0.033%.

Exercise:**Problem:**

Dry air consists of approximately 78% nitrogen, 21% oxygen, and 1% argon by mole, with trace amounts of other gases. A tank of compressed dry air has a volume of 1.76 cubic feet at a gauge pressure of 2200 pounds per square inch and a temperature of 293 K. How much oxygen does it contain in moles?

Solution:

65 mol

Exercise:**Problem:**

(a) Using data from the previous problem, find the mass of nitrogen, oxygen, and argon in 1 mol of dry air. The molar mass of N_2 is 28.0 g/mol, that of O_2 is 32.0 g/mol, and that of argon is 39.9 g/mol. (b) Dry air is mixed with pentane (C_5H_{12} , molar mass 72.2 g/mol), an important constituent of gasoline, in an air-fuel ratio of 15:1 by mass (roughly typical for car engines). Find the partial pressure of pentane in this mixture at an overall pressure of 1.00 atm.

Exercise:**Problem:**

(a) Given that air is 21 % oxygen, find the minimum atmospheric pressure that gives a relatively safe partial pressure of oxygen of 0.16 atm. (b) What is the minimum pressure that gives a partial pressure of oxygen above the quickly fatal level of 0.06 atm? (c) The air pressure at the summit of Mount Everest (8848 m) is 0.334 atm. Why have a few people climbed it without oxygen, while some who have tried, even though they had trained at high elevation, had to turn back?

Solution:

a. 0.76 atm; b. 0.29 atm; c. The pressure there is barely above the quickly fatal level.

Exercise:**Problem:**

(a) If the partial pressure of water vapor is 8.05 torr, what is the dew point? (760 torr = 1 atm = 101,325 Pa) (b) On a warm day when the air temperature is 35 °C and the dew point is 25 °C, what are the partial pressure of the water in the air and the relative humidity?

Glossary

Dalton's law of partial pressures

physical law that states that the total pressure of a gas is the sum of partial pressures of the component gases

internal energy

sum of the mechanical energies of all of the molecules in it

kinetic theory of gases

theory that derives the macroscopic properties of gases from the motion of the molecules they consist of

mean free path

average distance between collisions of a particle

mean free time

average time between collisions of a particle

partial pressure

pressure a gas would create if it occupied the total volume of space available

root-mean-square (rms) speed

square root of the average of the square (of a quantity)

vapor pressure

partial pressure of a vapor at which it is in equilibrium with the liquid (or solid, in the case of sublimation) phase of the same substance

Heat Capacity and Equipartition of Energy

By the end of this section, you will be able to:

- Solve problems involving heat transfer to and from ideal monatomic gases whose volumes are held constant
- Solve similar problems for non-monatomic ideal gases based on the number of degrees of freedom of a molecule
- Estimate the heat capacities of metals using a model based on degrees of freedom

In the chapter on temperature and heat, we defined the specific heat capacity with the equation $Q = mc\Delta T$, or $c = (1/m)Q/\Delta T$. However, the properties of an ideal gas depend directly on the number of moles in a sample, so here we define specific heat capacity in terms of the number of moles, not the mass. Furthermore, when talking about solids and liquids, we ignored any changes in volume and pressure with changes in temperature—a good approximation for solids and liquids, but for gases, we have to make some condition on volume or pressure changes. Here, we focus on the heat capacity with the volume held constant. We can calculate it for an ideal gas.

Heat Capacity of an Ideal Monatomic Gas at Constant Volume

We define the *molar heat capacity at constant volume* C_V as

Equation:

$$C_V = \frac{1}{n} \frac{Q}{\Delta T}, \text{ with } V \text{ held constant.}$$

This is often expressed in the form

Note:

Equation:

$$Q = nC_V\Delta T.$$

If the volume does not change, there is no overall displacement, so no work is done, and the only change in internal energy is due to the heat flow $\Delta E_{\text{int}} = Q$. (This statement is discussed further in the next chapter.) We use the equation

$E_{\text{int}} = 3nRT/2$ to write $\Delta E_{\text{int}} = 3nR\Delta T/2$ and substitute ΔE for Q to find $Q = 3nR\Delta T/2$, which gives the following simple result for an ideal monatomic gas:

Equation:

$$C_V = \frac{3}{2}R.$$

It is independent of temperature, which justifies our use of finite differences instead of a derivative. This formula agrees well with experimental results.

In the next chapter we discuss the molar specific heat at constant pressure C_p , which is always greater than C_V .

Example:

Calculating Temperature

A sample of 0.125 kg of xenon is contained in a rigid metal cylinder, big enough that the xenon can be modeled as an ideal gas, at a temperature of 20.0 °C. The cylinder is moved outside on a hot summer day. As the xenon comes into equilibrium by reaching the temperature of its surroundings, 180 J of heat are conducted to it through the cylinder walls. What is the equilibrium temperature? Ignore the expansion of the metal cylinder.

Solution

1. Identify the knowns: We know the initial temperature T_1 is 20.0 °C, the heat Q is 180 J, and the mass m of the xenon is 0.125 kg.
2. Identify the unknown. We need the final temperature, so we'll need ΔT .
3. Determine which equations are needed. Because xenon gas is monatomic, we can use $Q = 3nR\Delta T/2$. Then we need the number of moles, $n = m/M$.
4. Substitute the known values into the equations and solve for the unknowns. The molar mass of xenon is 131.3 g, so we obtain

Equation:

$$n = \frac{125 \text{ g}}{131.3 \text{ g/mol}} = 0.952 \text{ mol},$$

Equation:

$$\Delta T = \frac{2Q}{3nR} = \frac{2(180 \text{ J})}{3(0.952 \text{ mol})(8.31 \text{ J/mol} \cdot ^\circ\text{C})} = 15.2 ^\circ\text{C}.$$

Therefore, the final temperature is $35.2 ^\circ\text{C}$. The problem could equally well be solved in kelvin; as a kelvin is the same size as a degree Celsius of temperature change, you would get $\Delta T = 15.2 \text{ K}$.

Significance

The heating of an ideal or almost ideal gas at constant volume is important in car engines and many other practical systems.

Note:

Exercise:

Problem:

Check Your Understanding Suppose 2 moles of helium gas at 200 K are mixed with 2 moles of krypton gas at 400 K in a calorimeter. What is the final temperature?

Solution:

As the number of moles is equal and we know the molar heat capacities of the two gases are equal, the temperature is halfway between the initial temperatures, 300 K.

We would like to generalize our results to ideal gases with more than one atom per molecule. In such systems, the molecules can have other forms of energy beside translational kinetic energy, such as rotational kinetic energy and vibrational kinetic and potential energies. We will see that a simple rule lets us determine the average energies present in these forms and solve problems in much the same way as we have for monatomic gases.

Degrees of Freedom

In the previous section, we found that $\frac{1}{2}m\bar{v}^2 = \frac{3}{2}k_B T$ and $\bar{v}^2 = 3\bar{v}_x^2$, from which it follows that $\frac{1}{2}m\bar{v}_x^2 = \frac{1}{2}k_B T$. The same equation holds for \bar{v}_y^2 and for \bar{v}_z^2 . Thus, we can look at our energy of $\frac{3}{2}k_B T$ as the sum of contributions of $\frac{1}{2}k_B T$ from each of the three dimensions of translational motion. Shifting to the gas as a whole, we see that the 3 in the formula $C_V = \frac{3}{2}R$ also reflects those three dimensions. We define a **degree of freedom** as an independent possible motion of a molecule, such as each of the three dimensions of translation. Then, letting d represent the number of degrees of freedom, the molar heat capacity at constant volume of a monatomic ideal gas is $C_V = \frac{d}{2}R$, where $d = 3$.

The branch of physics called *statistical mechanics* tells us, and experiment confirms, that C_V of any ideal gas is given by this equation, regardless of the number of degrees of freedom. This fact follows from a more general result, the **equipartition theorem**, which holds in classical (non-quantum) thermodynamics for systems in thermal equilibrium under technical conditions that are beyond our scope. Here, we mention only that in a system, the energy is shared among the degrees of freedom by collisions.

Note:

Equipartition Theorem

The energy of a thermodynamic system in equilibrium is partitioned equally among its degrees of freedom. Accordingly, the molar heat capacity of an ideal gas is proportional to its number of degrees of freedom, d :

Equation:

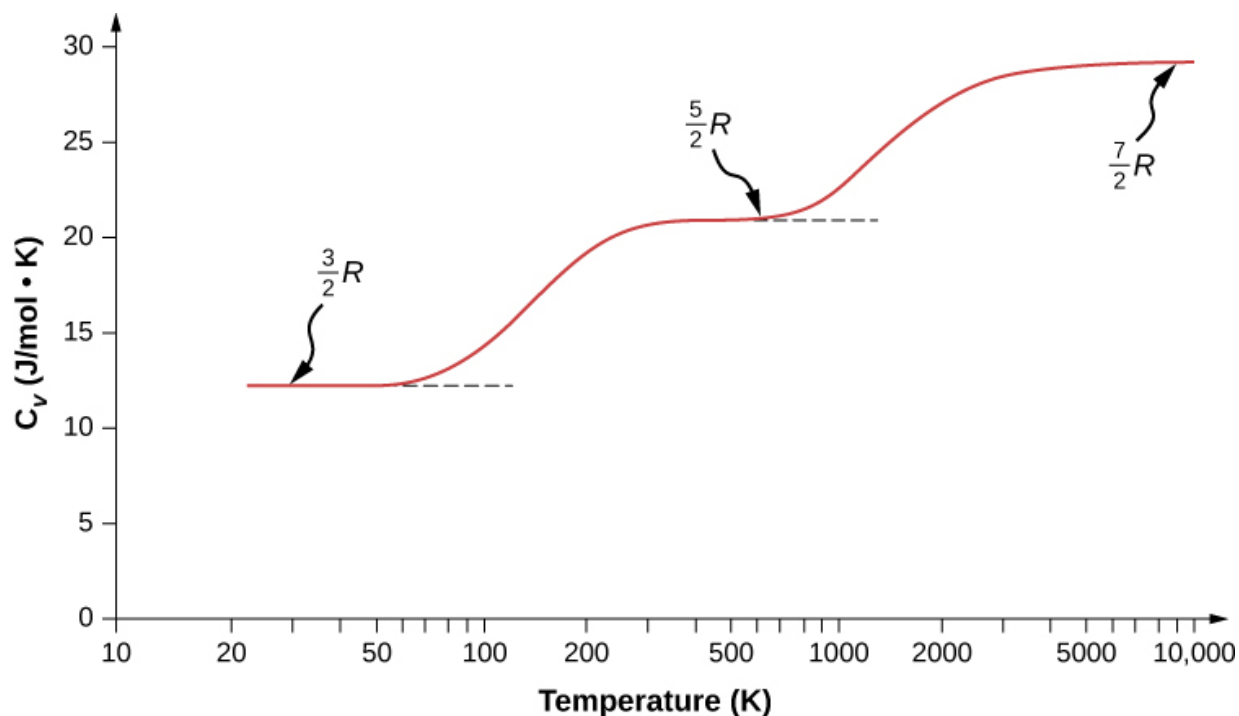
$$C_V = \frac{d}{2}R.$$

This result is due to the Scottish physicist James Clerk Maxwell (1831–1871), whose name will appear several more times in this book.

For example, consider a diatomic ideal gas (a good model for nitrogen, N_2 , and oxygen, O_2). Such a gas has more degrees of freedom than a monatomic gas. In addition to the three degrees of freedom for translation, it has two degrees of freedom for rotation perpendicular to its axis. Furthermore, the molecule can vibrate along its axis. This motion is often modeled by imagining a spring connecting the two atoms, and we know from simple harmonic motion that such motion has both kinetic and

potential energy. Each of these forms of energy corresponds to a degree of freedom, giving two more.

We might expect that for a diatomic gas, we should use 7 as the number of degrees of freedom; classically, if the molecules of a gas had only translational kinetic energy, collisions between molecules would soon make them rotate and vibrate. However, as explained in the previous module, quantum mechanics controls which degrees of freedom are active. The result is shown in [\[link\]](#). Both rotational and vibrational energies are limited to discrete values. For temperatures below about 60 K, the energies of hydrogen molecules are too low for a collision to bring the rotational state or vibrational state of a molecule from the lowest energy to the second lowest, so the only form of energy is translational kinetic energy, and $d = 3$ or $C_V = 3R/2$ as in a monatomic gas. Above that temperature, the two rotational degrees of freedom begin to contribute, that is, some molecules are excited to the rotational state with the second-lowest energy. (This temperature is much lower than that where rotations of monatomic gases contribute, because diatomic molecules have much higher rotational inertias and hence much lower rotational energies.) From about room temperature (a bit less than 300 K) to about 600 K, the rotational degrees of freedom are fully active, but the vibrational ones are not, and $d = 5$. Then, finally, above about 3000 K, the vibrational degrees of freedom are fully active, and $d = 7$ as the classical theory predicted.



The molar heat capacity of hydrogen as a function of temperature (on a logarithmic scale). The three “steps” or “plateaus” show different numbers of degrees of freedom that the typical energies of molecules must achieve to activate. Translational kinetic energy corresponds to three degrees of freedom, rotational to another two, and vibrational to yet another two.

Polyatomic molecules typically have one additional rotational degree of freedom at room temperature, since they have comparable moments of inertia around any axis. Thus, at room temperature, they have $d = 6$, and at high temperature, $d = 8$. We usually assume that gases have the theoretical room-temperature values of d .

As shown in [\[link\]](#), the results agree well with experiments for many monatomic and diatomic gases, but the agreement for triatomic gases is only fair. The differences arise from interactions that we have ignored between and within molecules.

Gas	C_V/R at 25 °C and 1 atm
Ar	1.50
He	1.50
Ne	1.50
CO	2.50
H ₂	2.47
N ₂	2.50
O ₂	2.53
F ₂	2.8
CO ₂	3.48

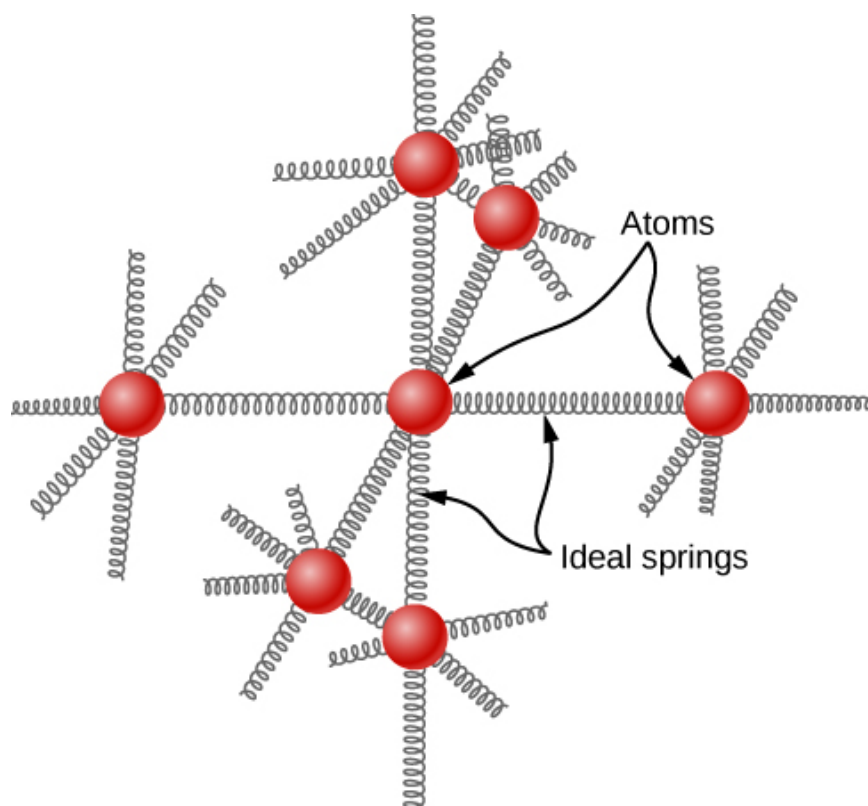
Gas	C_V/R at 25 °C and 1 atm
H ₂ S	3.13
N ₂ O	3.66

C_V/R for Various Monatomic, Diatomic, and Triatomic Gases

What about internal energy for diatomic and polyatomic gases? For such gases, C_V is a function of temperature ([\[link\]](#)), so we do not have the kind of simple result we have for monatomic ideal gases.

Molar Heat Capacity of Solid Elements

The idea of equipartition leads to an estimate of the molar heat capacity of solid elements at ordinary temperatures. We can model the atoms of a solid as attached to neighboring atoms by springs ([\[link\]](#)).



In a simple model of a solid element, each atom is

attached to others by six springs, two for each possible motion: x , y , and z . Each of the three motions corresponds to two degrees of freedom, one for kinetic energy and one for potential energy. Thus $d = 6$.

Analogously to the discussion of vibration in the previous module, each atom has six degrees of freedom: one kinetic and one potential for each of the x -, y -, and z -directions. Accordingly, the molar specific heat of a metal should be $3R$. This result, known as the Law of Dulong and Petit, works fairly well experimentally at room temperature. (For every element, it fails at low temperatures for quantum-mechanical reasons. Since quantum effects are particularly important for low-mass particles, the Law of Dulong and Petit already fails at room temperature for some light elements, such as beryllium and carbon. It also fails for some heavier elements for various reasons beyond what we can cover.)

Note:**Problem-Solving Strategy: Heat Capacity and Equipartition**

The strategy for solving these problems is the same as the one in [Phase Changes](#) for the effects of heat transfer. The only new feature is that you should determine whether the case just presented—ideal gases at constant volume—applies to the problem. (For solid elements, looking up the specific heat capacity is generally better than estimating it from the Law of Dulong and Petit.) In the case of an ideal gas, determine the number d of degrees of freedom from the number of atoms in the gas molecule and use it to calculate C_V (or use C_V to solve for d).

Example:**Calculating Temperature: Calorimetry with an Ideal Gas**

A 300-g piece of solid gallium (a metal used in semiconductor devices) at its melting point of only 30.0°C is in contact with 12.0 moles of air (assumed diatomic) at 95.0°C in an insulated container. When the air reaches equilibrium with the gallium, 202 g of the gallium have melted. Based on those data, what is the heat of fusion of gallium? Assume the volume of the air does not change and there are no other heat transfers.

Strategy

We'll use the equation $Q_{\text{hot}} + Q_{\text{cold}} = 0$. As some of the gallium doesn't melt, we know the final temperature is still the melting point. Then the only Q_{hot} is the heat

lost as the air cools, $Q_{\text{hot}} = n_{\text{air}} C_V \Delta T$, where $C_V = 5R/2$. The only Q_{cold} is the latent heat of fusion of the gallium, $Q_{\text{cold}} = m_{\text{Ga}} L_f$. It is positive because heat flows into the gallium.

Solution

1. Set up the equation:

Equation:

$$n_{\text{air}} C_V \Delta T + m_{\text{Ga}} L_f = 0.$$

2. Substitute the known values and solve:

Equation:

$$(12.0 \text{ mol}) \left(\frac{5}{2} \right) \left(8.31 \frac{\text{J}}{\text{mol} \cdot ^\circ\text{C}} \right) (30.0 ^\circ\text{C} - 95.0 ^\circ\text{C}) + (0.202 \text{ kg}) L_f = 0.$$

We solve to find that the heat of fusion of gallium is 80.2 kJ/kg.

Summary

- Every degree of freedom of an ideal gas contributes $\frac{1}{2} k_B T$ per atom or molecule to its changes in internal energy.
- Every degree of freedom contributes $\frac{1}{2} R$ to its molar heat capacity at constant volume C_V .
- Degrees of freedom do not contribute if the temperature is too low to excite the minimum energy of the degree of freedom as given by quantum mechanics. Therefore, at ordinary temperatures, $d = 3$ for monatomic gases, $d = 5$ for diatomic gases, and $d \approx 6$ for polyatomic gases.

Conceptual Questions

Exercise:

Problem:

Experimentally it appears that many polyatomic molecules' vibrational degrees of freedom can contribute to some extent to their energy at room temperature. Would you expect that fact to increase or decrease their heat capacity from the value R ? Explain.

Exercise:**Problem:**

One might think that the internal energy of diatomic gases is given by $E_{\text{int}} = 5RT/2$. Do diatomic gases near room temperature have more or less internal energy than that? *Hint:* Their internal energy includes the total energy added in raising the temperature from the boiling point (very low) to room temperature.

Solution:

Less, because at lower temperatures their heat capacity was only $3RT/2$.

Exercise:**Problem:**

You mix 5 moles of H_2 at 300 K with 5 moles of He at 360 K in a perfectly insulated calorimeter. Is the final temperature higher or lower than 330 K?

Problems**Exercise:****Problem:**

To give a helium atom nonzero angular momentum requires about 21.2 eV of energy (that is, 21.2 eV is the difference between the energies of the lowest-energy or ground state and the lowest-energy state with angular momentum). The electron-volt or eV is defined as 1.60×10^{-19} J. Find the temperature T where this amount of energy equals $k_{\text{B}}T/2$. Does this explain why we can ignore the rotational energy of helium for most purposes? (The results for other monatomic gases, and for diatomic gases rotating around the axis connecting the two atoms, have comparable orders of magnitude.)

Solution:

4.92×10^5 K; Yes, that's an impractically high temperature.

Exercise:

Problem:

(a) How much heat must be added to raise the temperature of 1.5 mol of air from $25.0\text{ }^{\circ}\text{C}$ to $33.0\text{ }^{\circ}\text{C}$ at constant volume? Assume air is completely diatomic. (b) Repeat the problem for the same number of moles of xenon, Xe.

Exercise:**Problem:**

A sealed, rigid container of 0.560 mol of an unknown ideal gas at a temperature of $30.0\text{ }^{\circ}\text{C}$ is cooled to $-40.0\text{ }^{\circ}\text{C}$. In the process, 980 J of heat are removed from the gas. Is the gas monatomic, diatomic, or polyatomic?

Solution:

polyatomic

Exercise:**Problem:**

A sample of neon gas (Ne, molar mass $M = 20.2\text{ g/mol}$) at a temperature of $13.0\text{ }^{\circ}\text{C}$ is put into a steel container of mass 47.2 g that's at a temperature of $-40.0\text{ }^{\circ}\text{C}$. The final temperature is $-28.0\text{ }^{\circ}\text{C}$. (No heat is exchanged with the surroundings, and you can neglect any change in the volume of the container.) What is the mass of the sample of neon?

Exercise:**Problem:**

A steel container of mass 135 g contains 24.0 g of ammonia, NH_3 , which has a molar mass of 17.0 g/mol. The container and gas are in equilibrium at $12.0\text{ }^{\circ}\text{C}$. How much heat has to be removed to reach a temperature of $-20.0\text{ }^{\circ}\text{C}$? Ignore the change in volume of the steel.

Solution:

$3.08 \times 10^3\text{ J}$

Exercise:

Problem:

A sealed room has a volume of 24 m^3 . It's filled with air, which may be assumed to be diatomic, at a temperature of 24°C and a pressure of $9.83 \times 10^4 \text{ Pa}$. A 1.00-kg block of ice at its melting point is placed in the room. Assume the walls of the room transfer no heat. What is the equilibrium temperature?

Exercise:**Problem:**

Heliox, a mixture of helium and oxygen, is sometimes given to hospital patients who have trouble breathing, because the low mass of helium makes it easier to breathe than air. Suppose helium at 25°C is mixed with oxygen at 35°C to make a mixture that is 70% helium by mole. What is the final temperature? Ignore any heat flow to or from the surroundings, and assume the final volume is the sum of the initial volumes.

Solution:

29.2°C

Exercise:**Problem:**

Professional divers sometimes use heliox, consisting of 79% helium and 21% oxygen by mole. Suppose a perfectly rigid scuba tank with a volume of 11 L contains heliox at an absolute pressure of $2.1 \times 10^7 \text{ Pa}$ at a temperature of 31°C . (a) How many moles of helium and how many moles of oxygen are in the tank? (b) The diver goes down to a point where the sea temperature is 27°C while using a negligible amount of the mixture. As the gas in the tank reaches this new temperature, how much heat is removed from it?

Exercise:

Problem:

In car racing, one advantage of mixing liquid nitrous oxide (N_2O) with air is that the boiling of the “nitrous” absorbs latent heat of vaporization and thus cools the air and ultimately the fuel-air mixture, allowing more fuel-air mixture to go into each cylinder. As a very rough look at this process, suppose 1.0 mol of nitrous oxide gas at its boiling point, -88°C , is mixed with 4.0 mol of air (assumed diatomic) at 30°C . What is the final temperature of the mixture? Use the measured heat capacity of N_2O at 25°C , which is $30.4\text{ J/mol }^\circ\text{C}$. (The primary advantage of nitrous oxide is that it consists of $1/3$ oxygen, which is more than air contains, so it supplies more oxygen to burn the fuel. Another advantage is that its decomposition into nitrogen and oxygen releases energy in the cylinder.)

Solution:

-1.6°C

Glossary

degree of freedom

independent kind of motion possessing energy, such as the kinetic energy of motion in one of the three orthogonal spatial directions

equipartition theorem

theorem that the energy of a classical thermodynamic system is shared equally among its degrees of freedom

Distribution of Molecular Speeds

By the end of this section, you will be able to:

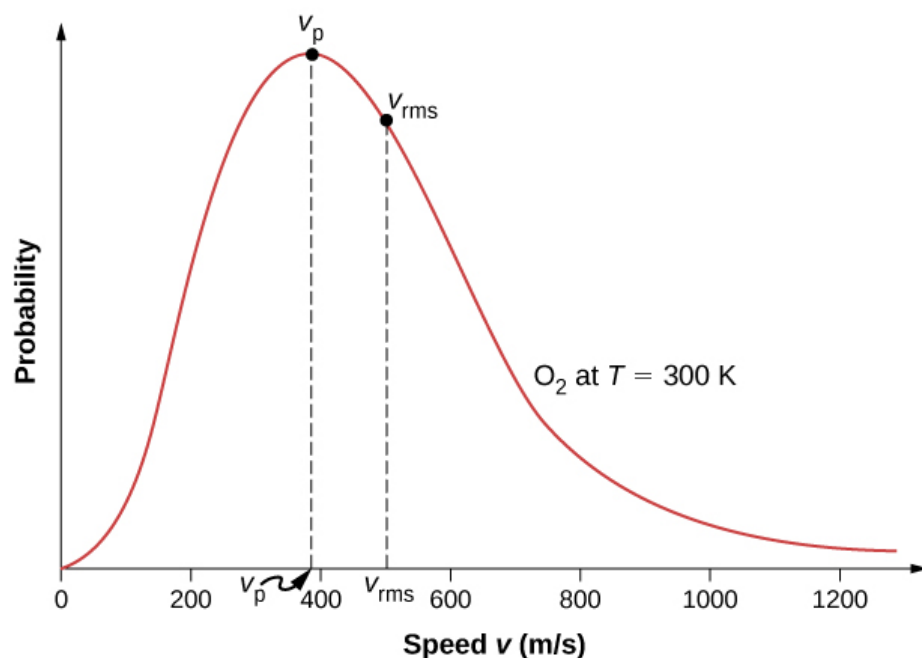
- Describe the distribution of molecular speeds in an ideal gas
- Find the average and most probable molecular speeds in an ideal gas

Particles in an ideal gas all travel at relatively high speeds, but they do not travel at the same speed. The rms speed is one kind of average, but many particles move faster and many move slower. The actual distribution of speeds has several interesting implications for other areas of physics, as we will see in later chapters.

The Maxwell-Boltzmann Distribution

The motion of molecules in a gas is random in magnitude and direction for individual molecules, but a gas of many molecules has a predictable distribution of molecular speeds. This predictable distribution of molecular speeds is known as the **Maxwell-Boltzmann distribution**, after its originators, who calculated it based on kinetic theory, and it has since been confirmed experimentally ([link](#)).

To understand this figure, we must define a distribution function of molecular speeds, since with a finite number of molecules, the probability that a molecule will have exactly a given speed is 0.



The Maxwell-Boltzmann distribution of molecular speeds in an ideal gas. The most likely speed v_p is less than the rms speed v_{rms} .

Although very high speeds are possible, only a tiny fraction of the molecules have speeds that are an order of magnitude greater than

v_{rms} .

We define the distribution function $f(v)$ by saying that the expected number $N(v_1, v_2)$ of particles with speeds between v_1 and v_2 is given by

Equation:

$$N(v_1, v_2) = N \int_{v_1}^{v_2} f(v) dv.$$

[Since N is dimensionless, the unit of $f(v)$ is seconds per meter.] We can write this equation conveniently in differential form:

Equation:

$$dN = N f(v) dv.$$

In this form, we can understand the equation as saying that the number of molecules with speeds between v and $v + dv$ is the total number of molecules in the sample times $f(v)$ times dv . That is, the probability that a molecule's speed is between v and $v + dv$ is $f(v)dv$.

We can now quote Maxwell's result, although the proof is beyond our scope.

Note:

Maxwell-Boltzmann Distribution of Speeds

The distribution function for speeds of particles in an ideal gas at temperature T is

Equation:

$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}.$$

The factors before the v^2 are a normalization constant; they make sure that $N(0, \infty) = N$ by making sure that $\int_0^\infty f(v) dv = 1$. Let's focus on the dependence on v . The factor of v^2 means that $f(0) = 0$ and for small v , the curve looks like a parabola. The factor of $e^{-mv^2/2k_B T}$ means that $\lim_{v \rightarrow \infty} f(v) = 0$ and the graph has an exponential tail, which indicates that a few molecules may move at several times the rms speed. The interaction of these factors gives the function the single-peaked shape shown in the figure.

Example:

Calculating the Ratio of Numbers of Molecules Near Given Speeds

In a sample of nitrogen (N_2 , with a molar mass of 28.0 g/mol) at a temperature of 273 °C, find the ratio of the number of molecules with a speed very close to 300 m/s to the number with a speed very

close to 100 m/s.

Strategy

Since we're looking at a small range, we can approximate the number of molecules near 100 m/s as $dN_{100} = f(100 \text{ m/s})dv$. Then the ratio we want is

Equation:

$$\frac{dN_{300}}{dN_{100}} = \frac{f(300 \text{ m/s})dv}{f(100 \text{ m/s})dv} = \frac{f(300 \text{ m/s})}{f(100 \text{ m/s})}.$$

All we have to do is take the ratio of the two f values.

Solution

1. Identify the knowns and convert to SI units if necessary.

Equation:

$$T = 300 \text{ K}, k_B = 1.38 \times 10^{-23} \text{ J/K}$$

Equation:

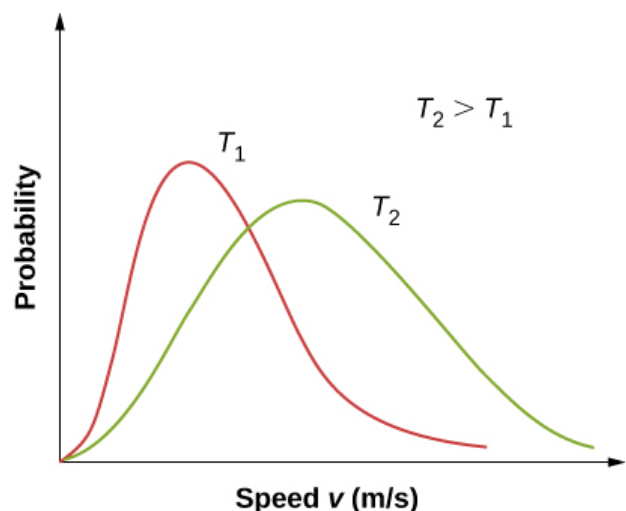
$$M = 0.0280 \text{ kg/mol so } m = 4.65 \times 10^{-26} \text{ kg}$$

2. Substitute the values and solve.

Equation:

$$\begin{aligned} \frac{f(300 \text{ m/s})}{f(100 \text{ m/s})} &= \frac{\frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} (300 \text{ m/s})^2 \exp[-m(300 \text{ m/s})^2/2k_B T]}{\frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} (100 \text{ m/s})^2 \exp[-m(100 \text{ m/s})^2/2k_B T]} \\ &= \frac{(300 \text{ m/s})^2 \exp[-(4.65 \times 10^{-26} \text{ kg})(300 \text{ m/s})^2/2(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})]}{(100 \text{ m/s})^2 \exp[-(4.65 \times 10^{-26} \text{ kg})(100 \text{ m/s})^2/2(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})]} \\ &= 3^2 \exp \left[-\frac{(4.65 \times 10^{-26} \text{ kg})[(300 \text{ m/s})^2 - (100 \text{ m/s})^2]}{2(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})} \right] \\ &= 5.74 \end{aligned}$$

[\[link\]](#) shows that the curve is shifted to higher speeds at higher temperatures, with a broader range of speeds.



The Maxwell-Boltzmann distribution is shifted to higher speeds and broadened at higher temperatures.

Note:

With only a relatively small number of molecules, the distribution of speeds fluctuates around the Maxwell-Boltzmann distribution. However, you can view this [simulation](#) to see the essential features that more massive molecules move slower and have a narrower distribution. Use the set-up “2 Gases, Random Speeds”. Note the display at the bottom comparing histograms of the speed distributions with the theoretical curves.

We can use a probability distribution to calculate average values by multiplying the distribution function by the quantity to be averaged and integrating the product over all possible speeds. (This is analogous to calculating averages of discrete distributions, where you multiply each value by the number of times it occurs, add the results, and divide by the number of values. The integral is analogous to the first two steps, and the normalization is analogous to dividing by the number of values.) Thus the average velocity is

Note:

Equation:

$$\bar{v} = \int_0^{\infty} v f(v) dv = \sqrt{\frac{8}{\pi} \frac{k_B T}{m}} = \sqrt{\frac{8}{\pi} \frac{RT}{M}}.$$

Similarly,

Equation:

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\int_0^\infty v^2 f(v) dv} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

as in [Pressure, Temperature, and RMS Speed](#). The **most probable speed**, also called the **peak speed** v_p , is the speed at the peak of the velocity distribution. (In statistics it would be called the mode.) It is less than the rms speed v_{rms} . The most probable speed can be calculated by the more familiar method of setting the derivative of the distribution function, with respect to v , equal to 0. The result is

Note:

Equation:

$$v_p = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}},$$

which is less than v_{rms} . In fact, the rms speed is greater than both the most probable speed and the average speed.

The peak speed provides a sometimes more convenient way to write the Maxwell-Boltzmann distribution function:

Equation:

$$f(v) = \frac{4v^2}{\sqrt{\pi}v_p^3} e^{-v^2/v_p^2}$$

In the factor $e^{-mv^2/2k_B T}$, it is easy to recognize the translational kinetic energy. Thus, that expression is equal to $e^{-K/k_B T}$. The distribution $f(v)$ can be transformed into a kinetic energy distribution by requiring that $f(K)dK = f(v)dv$. Boltzmann showed that the resulting formula is much more generally applicable if we replace the kinetic energy of translation with the total mechanical energy E . Boltzmann's result is

Equation:

$$f(E) = \frac{2}{\sqrt{\pi}} (k_B T)^{-3/2} \sqrt{E} e^{-E/k_B T} = \frac{2}{\sqrt{\pi} (k_B T)^{3/2}} \frac{\sqrt{E}}{e^{E/k_B T}}.$$

The first part of this equation, with the negative exponential, is the usual way to write it. We give the second part only to remark that $e^{E/k_B T}$ in the denominator is ubiquitous in quantum as well as classical statistical mechanics.

Note:**Problem-Solving Strategy: Speed Distribution**

Step 1. Examine the situation to determine that it relates to the distribution of molecular speeds.

Step 2. Make a list of what quantities are given or can be inferred from the problem as stated (identify the known quantities).

Step 3. Identify exactly what needs to be determined in the problem (identify the unknown quantities). A written list is useful.

Step 4. Convert known values into proper SI units (K for temperature, Pa for pressure, m^3 for volume, molecules for N , and moles for n). In many cases, though, using R and the molar mass will be more convenient than using k_B and the molecular mass.

Step 5. Determine whether you need the distribution function for velocity or the one for energy, and whether you are using a formula for one of the characteristic speeds (average, most probably, or rms), finding a ratio of values of the distribution function, or approximating an integral.

Step 6. Solve the appropriate equation for the ideal gas law for the quantity to be determined (the unknown quantity). Note that if you are taking a ratio of values of the distribution function, the normalization factors divide out. Or if approximating an integral, use the method asked for in the problem.

Step 7. Substitute the known quantities, along with their units, into the appropriate equation and obtain numerical solutions complete with units.

We can now gain a qualitative understanding of a puzzle about the composition of Earth's atmosphere. Hydrogen is by far the most common element in the universe, and helium is by far the second-most common. Moreover, helium is constantly produced on Earth by radioactive decay. Why are those elements so rare in our atmosphere? The answer is that gas molecules that reach speeds above Earth's escape velocity, about 11 km/s, can escape from the atmosphere into space. Because of the lower mass of hydrogen and helium molecules, they move at higher speeds than other gas molecules, such as nitrogen and oxygen. Only a few exceed escape velocity, but far fewer heavier molecules do. Thus, over the billions of years that Earth has existed, far more hydrogen and helium molecules have escaped from the atmosphere than other molecules, and hardly any of either is now present.

We can also now take another look at evaporative cooling, which we discussed in the chapter on temperature and heat. Liquids, like gases, have a distribution of molecular energies. The highest-energy molecules are those that can escape from the intermolecular attractions of the liquid. Thus, when some liquid evaporates, the molecules left behind have a lower average energy, and the liquid has a lower temperature.

Summary

- The motion of individual molecules in a gas is random in magnitude and direction. However, a gas of many molecules has a predictable distribution of molecular speeds, known as the Maxwell-Boltzmann distribution.
- The average and most probable velocities of molecules having the Maxwell-Boltzmann speed distribution, as well as the rms velocity, can be calculated from the temperature and molecular mass.

Key Equations

Ideal gas law in terms of molecules	$pV = Nk_{\text{B}}T$
Ideal gas law ratios if the amount of gas is constant	$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$
Ideal gas law in terms of moles	$pV = nRT$
Van der Waals equation	$\left[p + a\left(\frac{n}{V}\right)^2 \right] (V - nb) = nRT$
Pressure, volume, and molecular speed	$pV = \frac{1}{3}Nm\bar{v}^2$
Root-mean-square speed	$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_{\text{B}}T}{m}}$
Mean free path	$\lambda = \frac{V}{4\sqrt{2}\pi r^2 N} = \frac{k_{\text{B}}T}{4\sqrt{2}\pi r^2 p}$
Mean free time	$\tau = \frac{k_{\text{B}}T}{4\sqrt{2}\pi r^2 p v_{\text{rms}}}$
The following two equations apply only to a monatomic ideal gas:	
Average kinetic energy of a molecule	$\bar{K} = \frac{3}{2}k_{\text{B}}T$
Internal energy	$E_{\text{int}} = \frac{3}{2}Nk_{\text{B}}T.$
Heat in terms of molar heat capacity at constant volume	$Q = nC_V\Delta T$
Molar heat capacity at constant volume for an ideal gas with d degrees of freedom	$C_V = \frac{d}{2}R$
Maxwell–Boltzmann speed distribution	$f(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_{\text{B}}T}\right)^{3/2}v^2e^{-mv^2/2k_{\text{B}}T}$
Average velocity of a molecule	$\bar{v} = \sqrt{\frac{8}{\pi}\frac{k_{\text{B}}T}{m}} = \sqrt{\frac{8}{\pi}\frac{RT}{M}}$
Peak velocity of a molecule	$v_p = \sqrt{\frac{2k_{\text{B}}T}{m}} = \sqrt{\frac{2RT}{M}}$

Conceptual Questions

Exercise:

Problem:

One cylinder contains helium gas and another contains krypton gas at the same temperature. Mark each of these statements true, false, or impossible to determine from the given information. (a) The rms speeds of atoms in the two gases are the same. (b) The average kinetic energies of atoms in the two gases are the same. (c) The internal energies of 1 mole of gas in each cylinder are the same. (d) The pressures in the two cylinders are the same.

Solution:

a. false; b. true; c. true; d. true

Exercise:**Problem:**

Repeat the previous question if one gas is still helium but the other is changed to fluorine, F_2 .

Exercise:**Problem:**

An ideal gas is at a temperature of 300 K. To double the average speed of its molecules, what does the temperature need to be changed to?

Solution:

1200 K

Problems**Exercise:****Problem:**

In a sample of hydrogen sulfide ($M = 34.1$ g/mol) at a temperature of 3.00×10^2 K, estimate the ratio of the number of molecules that have speeds very close to v_{rms} to the number that have speeds very close to $2v_{\text{rms}}$.

Exercise:**Problem:**

Using the approximation $\int_{v_1}^{v_1+\Delta v} f(v)dv \approx f(v_1)\Delta v$ for small Δv , estimate the fraction of nitrogen molecules at a temperature of 3.00×10^2 K that have speeds between 290 m/s and 291 m/s.

Solution:

0.00157

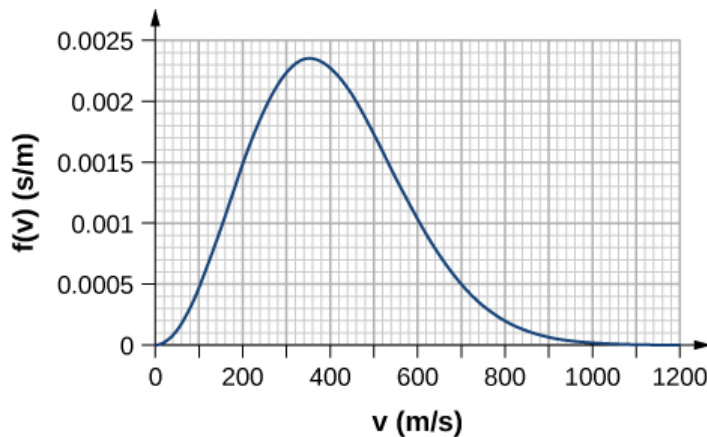
Exercise:

Problem:

Using the method of the preceding problem, estimate the fraction of nitric oxide (NO) molecules at a temperature of 250 K that have energies between 3.45×10^{-21} J and 3.50×10^{-21} J.

Exercise:**Problem:**

By counting squares in the following figure, estimate the fraction of argon atoms at $T = 300$ K that have speeds between 600 m/s and 800 m/s. The curve is correctly normalized. The value of a square is its length as measured on the x -axis times its height as measured on the y -axis, with the units given on those axes.



Solution:

About 0.072. Answers may vary slightly. A more accurate answer is 0.074.

Exercise:**Problem:**

Using a numerical integration method such as Simpson's rule, find the fraction of molecules in a sample of oxygen gas at a temperature of 250 K that have speeds between 100 m/s and 150 m/s. The molar mass of oxygen (O_2) is 32.0 g/mol. A precision to two significant digits is enough.

Exercise:**Problem:**

Find (a) the most probable speed, (b) the average speed, and (c) the rms speed for nitrogen molecules at 295 K.

Solution:

a. 419 m/s; b. 472 m/s; c. 513 m/s

Exercise:

Problem: Repeat the preceding problem for nitrogen molecules at 2950 K.

Exercise:

Problem:

At what temperature is the average speed of carbon dioxide molecules ($M = 44.0 \text{ g/mol}$) 510 m/s?

Solution:

541 K

Exercise:

Problem:

The most probable speed for molecules of a gas at 296 K is 263 m/s. What is the molar mass of the gas? (You might like to figure out what the gas is likely to be.)

Exercise:

Problem:

a) At what temperature do oxygen molecules have the same average speed as helium atoms ($M = 4.00 \text{ g/mol}$) have at 300 K? b) What is the answer to the same question about most probable speeds? c) What is the answer to the same question about rms speeds?

Solution:

2400 K for all three parts

Additional Problems

Exercise:

Problem:

In the deep space between galaxies, the density of molecules (which are mostly single atoms) can be as low as 10^6 atoms/m^3 , and the temperature is a frigid 2.7 K. What is the pressure? (b) What volume (in m^3) is occupied by 1 mol of gas? (c) If this volume is a cube, what is the length of its sides in kilometers?

Exercise:

Problem:

(a) Find the density in SI units of air at a pressure of 1.00 atm and a temperature of 20°C , assuming that air is 78% N_2 , 21% O_2 , and 1% Ar, (b) Find the density of the atmosphere on Venus, assuming that it's 96% CO_2 and 4% N_2 , with a temperature of 737 K and a pressure of 92.0 atm.

Solution:

a. 1.20 kg/m^3 ; b. 65.9 kg/m^3

Exercise:

Problem:

The air inside a hot-air balloon has a temperature of 370 K and a pressure of 101.3 kPa, the same as that of the air outside. Using the composition of air as 78% N_2 , 21% O_2 , and 1% Ar, find the density of the air inside the balloon.

Exercise:

Problem:

When an air bubble rises from the bottom to the top of a freshwater lake, its volume increases by 80 %. If the temperatures at the bottom and the top of the lake are 4.0 and 10 °C, respectively, how deep is the lake?

Solution:

7.9 m

Exercise:

Problem:

(a) Use the ideal gas equation to estimate the temperature at which 1.00 kg of steam (molar mass $M = 18.0 \text{ g/mol}$) at a pressure of $1.50 \times 10^6 \text{ Pa}$ occupies a volume of 0.220 m^3 . (b) The van der Waals constants for water are $a = 0.5537 \text{ Pa} \cdot \text{m}^6/\text{mol}^2$ and $b = 3.049 \times 10^{-5} \text{ m}^3/\text{mol}$. Use the Van der Waals equation of state to estimate the temperature under the same conditions. (c) The actual temperature is 779 K. Which estimate is better?

Exercise:

Problem:

One process for decaffeinating coffee uses carbon dioxide ($M = 44.0 \text{ g/mol}$) at a molar density of about $14,600 \text{ mol/m}^3$ and a temperature of about 60 °C. (a) Is CO_2 a solid, liquid, gas, or supercritical fluid under those conditions? (b) The van der Waals constants for carbon dioxide are $a = 0.3658 \text{ Pa} \cdot \text{m}^6/\text{mol}^2$ and $b = 4.286 \times 10^{-5} \text{ m}^3/\text{mol}$. Using the van der Waals equation, estimate the pressure of CO_2 at that temperature and density.

Solution:

a. supercritical fluid; b. $3.00 \times 10^7 \text{ Pa}$

Exercise:

Problem:

On a winter day when the air temperature is 0 °C, the relative humidity is 50 %. Outside air comes inside and is heated to a room temperature of 20 °C. What is the relative humidity of the air inside the room. (Does this problem show why inside air is so dry in winter?)

Exercise:

Problem:

On a warm day when the air temperature is $30\text{ }^{\circ}\text{C}$, a metal can is slowly cooled by adding bits of ice to liquid water in it. Condensation first appears when the can reaches $15\text{ }^{\circ}\text{C}$. What is the relative humidity of the air?

Solution:

40.18 %

Exercise:**Problem:**

(a) People often think of humid air as “heavy.” Compare the densities of air with 0% relative humidity and 100% relative humidity when both are at 1 atm and $30\text{ }^{\circ}\text{C}$. Assume that the dry air is an ideal gas composed of molecules with a molar mass of 29.0 g/mol and the moist air is the same gas mixed with water vapor. (b) As discussed in the chapter on the applications of Newton’s laws, the air resistance felt by projectiles such as baseballs and golf balls is approximately $F_D = C\rho Av^2/2$, where ρ is the mass density of the air, A is the cross-sectional area of the projectile, and C is the projectile’s drag coefficient. For a fixed air pressure, describe qualitatively how the range of a projectile changes with the relative humidity. (c) When a thunderstorm is coming, usually the humidity is high and the air pressure is low. Do those conditions give an advantage or disadvantage to home-run hitters?

Exercise:**Problem:**

The mean free path for helium at a certain temperature and pressure is $2.10 \times 10^{-7}\text{ m}$. The radius of a helium atom can be taken as $1.10 \times 10^{-11}\text{ m}$. What is the measure of the density of helium under those conditions (a) in molecules per cubic meter and (b) in moles per cubic meter?

Solution:

a. $2.21 \times 10^{27}\text{ molecules/m}^3$; b. $3.67 \times 10^3\text{ mol/m}^3$

Exercise:**Problem:**

The mean free path for methane at a temperature of 269 K and a pressure of $1.11 \times 10^5\text{ Pa}$ is $4.81 \times 10^{-8}\text{ m}$. Find the effective radius r of the methane molecule.

Exercise:

Problem:

In the chapter on fluid mechanics, Bernoulli's equation for the flow of incompressible fluids was explained in terms of changes affecting a small volume dV of fluid. Such volumes are a fundamental idea in the study of the flow of compressible fluids such as gases as well. For the equations of hydrodynamics to apply, the mean free path must be much less than the linear size of such a volume, $a \approx dV^{1/3}$. For air in the stratosphere at a temperature of 220 K and a pressure of 5.8 kPa, how big should a be for it to be 100 times the mean free path? Take the effective radius of air molecules to be 1.88×10^{-11} m, which is roughly correct for N_2 .

Solution:

8.2 mm

Exercise:**Problem:**

Find the total number of collisions between molecules in 1.00 s in 1.00 L of nitrogen gas at standard temperature and pressure (0 °C, 1.00 atm). Use 1.88×10^{-10} m as the effective radius of a nitrogen molecule. (The number of collisions per second is the reciprocal of the collision time.) Keep in mind that each collision involves two molecules, so if one molecule collides once in a certain period of time, the collision of the molecule it hit cannot be counted.

Exercise:**Problem:**

(a) Estimate the specific heat capacity of sodium from the Law of Dulong and Petit. The molar mass of sodium is 23.0 g/mol. (b) What is the percent error of your estimate from the known value, 1230 J/kg · °C?

Solution:

a. 1080 J/kg · °C; b. 12 %

Exercise:**Problem:**

A sealed, perfectly insulated container contains 0.630 mol of air at 20.0 °C and an iron stirring bar of mass 40.0 g. The stirring bar is magnetically driven to a kinetic energy of 50.0 J and allowed to slow down by air resistance. What is the equilibrium temperature?

Exercise:**Problem:**

Find the ratio $f(v_p)/f(v_{rms})$ for hydrogen gas ($M = 2.02$ g/mol) at a temperature of 77.0 K.

Solution:

$2\sqrt{e}/3$ or about 1.10

Exercise:

Problem:

Unreasonable results. (a) Find the temperature of 0.360 kg of water, modeled as an ideal gas, at a pressure of 1.01×10^5 Pa if it has a volume of 0.615 m^3 . (b) What is unreasonable about this answer? How could you get a better answer?

Exercise:**Problem:**

Unreasonable results. (a) Find the average speed of hydrogen sulfide, H_2S , molecules at a temperature of 250 K. Its molar mass is 31.4 g/mol (b) The result isn't very unreasonable, but why is it less reliable than those for, say, neon or nitrogen?

Solution:

a. 411 m/s; b. According to [\[link\]](#), the C_V of H_2S is significantly different from the theoretical value, so the ideal gas model does not describe it very well at room temperature and pressure, and the Maxwell-Boltzmann speed distribution for ideal gases may not hold very well, even less well at a lower temperature.

Challenge Problems**Exercise:****Problem:**

An airtight dispenser for drinking water is $25 \text{ cm} \times 10 \text{ cm}$ in horizontal dimensions and 20 cm tall. It has a tap of negligible volume that opens at the level of the bottom of the dispenser. Initially, it contains water to a level 3.0 cm from the top and air at the ambient pressure, 1.00 atm, from there to the top. When the tap is opened, water will flow out until the gauge pressure at the bottom of the dispenser, and thus at the opening of the tap, is 0. What volume of water flows out? Assume the temperature is constant, the dispenser is perfectly rigid, and the water has a constant density of 1000 kg/m^3 .

Exercise:**Problem:**

Eight bumper cars, each with a mass of 322 kg, are running in a room 21.0 m long and 13.0 m wide. They have no drivers, so they just bounce around on their own. The rms speed of the cars is 2.50 m/s. Repeating the arguments of [Pressure, Temperature, and RMS Speed](#), find the average force per unit length (analogous to pressure) that the cars exert on the walls.

Solution:

29.5 N/m

Exercise:

Problem: Verify that $v_p = \sqrt{\frac{2k_B T}{m}}$.

Exercise:**Problem:**

Verify the normalization equation $\int_0^\infty f(v)dv = 1$. In doing the integral, first make the substitution $u = \sqrt{\frac{m}{2k_B T}} v = \frac{v}{v_p}$. This “scaling” transformation gives you all features of the answer except for the integral, which is a dimensionless numerical factor. You’ll need the formula

$$\int_0^\infty x^2 e^{-x^2} dx = \frac{\sqrt{\pi}}{4}$$

to find the numerical factor and verify the normalization.

Solution:

Substituting $v = \sqrt{\frac{2k_B T}{m}} u$ and $dv = \sqrt{\frac{2k_B T}{m}} du$ gives

$$\begin{aligned} \int_0^\infty \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T} dv &= \int_0^\infty \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} \left(\frac{2k_B T}{m} \right) u^2 e^{-u^2} \sqrt{\frac{2k_B T}{m}} du \\ &= \int_0^\infty \frac{4}{\sqrt{\pi}} u^2 e^{-u^2} du = \frac{4}{\sqrt{\pi}} \frac{\sqrt{\pi}}{4} = 1 \end{aligned}$$

Exercise:**Problem:**

Verify that $\bar{v} = \sqrt{\frac{8}{\pi} \frac{k_B T}{m}}$. Make the same scaling transformation as in the preceding problem.

Exercise:

Problem: Verify that $v_{\text{rms}} = \sqrt{\bar{v^2}} = \sqrt{\frac{3k_B T}{m}}$.

Solution:

Making the scaling transformation as in the previous problems, we find that

$$\bar{v^2} = \int_0^\infty \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} v^2 v^2 e^{-mv^2/2k_B T} dv = \int_0^\infty \frac{4}{\sqrt{\pi}} \frac{2k_B T}{m} u^4 e^{-u^2} du.$$

As in the previous problem, we integrate by parts:

$$\int_0^\infty u^4 e^{-u^2} du = \left[-\frac{1}{2} u^3 e^{-u^2} \right]_0^\infty + \frac{3}{2} \int_0^\infty u^2 e^{-u^2} du.$$

Again, the first term is 0, and we were given in an earlier problem that the integral in the second term equals $\frac{\sqrt{\pi}}{4}$. We now have

$$\bar{v^2} = \frac{4}{\sqrt{\pi}} \frac{2k_B T}{m} \frac{3}{2} \frac{\sqrt{\pi}}{4} = \frac{3k_B T}{m}.$$

Taking the square root of both sides gives the desired result: $v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}$.

Glossary

Maxwell-Boltzmann distribution

function that can be integrated to give the probability of finding ideal gas molecules with speeds in the range between the limits of integration

most probable speed

speed near which the speeds of most molecules are found, the peak of the speed distribution function

peak speed

same as “most probable speed”

Introduction

class="introduction"

A weak cold front of air pushes all the smog in northeastern China into a giant smog blanket over the Yellow Sea, as captured by NASA's Terra satellite in 2012. To understand changes in weather and climate, such as the event shown here, you need a thorough knowledge of thermodynamics . (credit: modification of work by NASA)



Heat is the transfer of energy due to a temperature difference between two systems. Heat describes the process of converting from one form of energy into another. A car engine, for example, burns gasoline. Heat is produced when the burned fuel is chemically transformed into mostly CO_2 and H_2O , which are gases at the combustion temperature. These gases exert a force on a piston through a displacement, doing work and converting the piston's kinetic energy into a variety of other forms—into the car's kinetic energy; into electrical energy to run the spark plugs, radio, and lights; and back into stored energy in the car's battery.

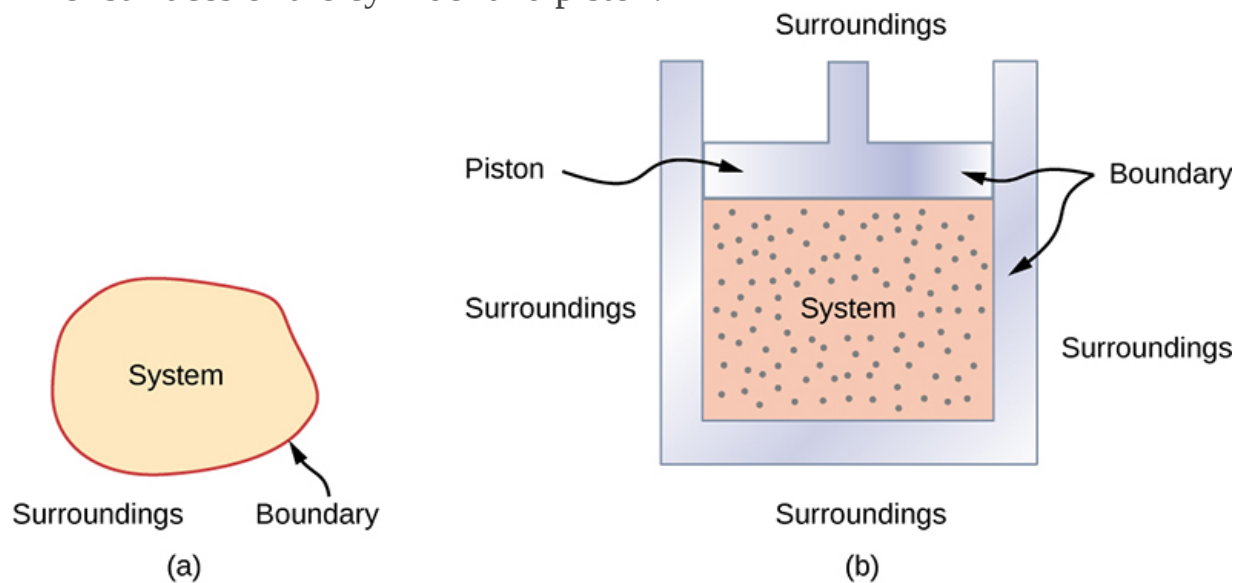
Energy is conserved in all processes, including those associated with thermodynamic systems. The roles of heat transfer and internal energy change vary from process to process and affect how work is done by the system in that process. We will see that the first law of thermodynamics explains that a change in the internal energy of a system comes from changes in heat or work. Understanding the laws that govern thermodynamic processes and the relationship between the system and its surroundings is therefore paramount in gaining scientific knowledge of energy and energy consumption.

Thermodynamic Systems

By the end of this section, you will be able to:

- Define a thermodynamic system, its boundary, and its surroundings
- Explain the roles of all the components involved in thermodynamics
- Define thermal equilibrium and thermodynamic temperature
- Link an equation of state to a system

A **thermodynamic system** includes anything whose thermodynamic properties are of interest. It is embedded in its **surroundings** or **environment**; it can exchange heat with, and do work on, its environment through a **boundary**, which is the imagined wall that separates the system and the environment ([\[link\]](#)). In reality, the immediate surroundings of the system are interacting with it directly and therefore have a much stronger influence on its behavior and properties. For example, if we are studying a car engine, the burning gasoline inside the cylinder of the engine is the thermodynamic system; the piston, exhaust system, radiator, and air outside form the surroundings of the system. The boundary then consists of the inner surfaces of the cylinder and piston.



- (a) A system, which can include any relevant process or value, is self-contained in an area. The surroundings may also have relevant information; however, the surroundings are important to study only if the situation is an open system. (b) The burning gasoline in the cylinder of a car engine is an example of a thermodynamic system.

Normally, a system must have some interactions with its surroundings. A system is called an isolated or **closed system** if it is completely separated from its environment—for example, a gas that is surrounded by immovable and thermally insulating walls. In reality, a closed system does not exist unless the entire universe is treated as the system, or it is used as a model for an actual system that has minimal interactions with its environment. Most systems are known as an **open system**, which can exchange energy and/or matter with its surroundings ([\[link\]](#)).



(a)



(b)

(a) This boiling tea kettle is an open thermodynamic system. It transfers heat and matter (steam) to its surroundings. (b) A pressure cooker is a good approximation to a closed system. A little steam escapes through the top valve to prevent explosion. (credit a: modification of work by Gina Hamilton; credit b: modification of work by Jane Whitney)

When we examine a thermodynamic system, we ignore the difference in behavior from place to place inside the system for a given moment. In other words, we concentrate on the macroscopic properties of the system, which are the averages of the microscopic properties of all the molecules or entities in the system. Any thermodynamic system is therefore treated as a continuum that has the same behavior everywhere inside. We assume the system is in **equilibrium**. You could have, for example, a temperature gradient across the system. However, when we discuss a thermodynamic system in this chapter, we study those that have uniform properties throughout the system.

Before we can carry out any study on a thermodynamic system, we need a fundamental characterization of the system. When we studied a mechanical system, we focused on the forces and torques on the system, and their balances dictated the mechanical equilibrium of the system. In a similar way, we should examine the heat transfer between a thermodynamic system and its environment or between the different parts of the system, and its balance should dictate the thermal equilibrium of the system. Intuitively, such a balance is reached if the temperature becomes the same for different objects or parts of the system in thermal contact, and the net heat transfer over time becomes zero.

Thus, when we say two objects (a thermodynamic system and its environment, for example) are in thermal equilibrium, we mean that they are at the same temperature, as we discussed in [Temperature and Heat](#). Let us consider three objects at temperatures T_1 , T_2 , and T_3 , respectively. How do we know whether they are in thermal equilibrium? The governing principle here is the zeroth law of thermodynamics, as described in [Temperature and Heat](#) on temperature and heat:

If object 1 is in thermal equilibrium with objects 2 and 3, respectively, then objects 2 and 3 must also be in thermal equilibrium.

Mathematically, we can simply write the zeroth law of thermodynamics as **Equation:**

$$\text{If } T_1 = T_2 \text{ and } T_1 = T_3, \text{ then } T_2 = T_3.$$

This is the most fundamental way of defining temperature: Two objects must be at the same temperature thermodynamically if the net heat transfer between them is zero when they are put in thermal contact and have reached a thermal equilibrium.

The zeroth law of thermodynamics is equally applicable to the different parts of a closed system and requires that the temperature everywhere inside the system be the same if the system has reached a thermal equilibrium. To simplify our discussion, we assume the system is uniform with only one type of material—for example, water in a tank. The measurable properties of the system at least include its volume, pressure, and temperature. The range of specific relevant variables depends upon the system. For example, for a stretched rubber band, the relevant variables would be length, tension, and temperature. The relationship between these three basic properties of the system is called the **equation of state** of the system and is written symbolically *for a closed system* as

Note:
Equation:

$$f(p, V, T) = 0,$$

where V , p , and T are the volume, pressure, and temperature of the system at a given condition.

In principle, this equation of state exists for any thermodynamic system but is not always readily available. The forms of $f(p, V, T) = 0$ for many materials have been determined either experimentally or theoretically. In the preceding chapter, we saw an example of an equation of state for an ideal gas, $f(p, V, T) = pV - nRT = 0$.

We have so far introduced several physical properties that are relevant to the thermodynamics of a thermodynamic system, such as its volume,

pressure, and temperature. We can separate these quantities into two generic categories. The quantity associated with an amount of matter is an **extensive variable**, such as the volume and the number of moles. The other properties of a system are **intensive variables**, such as the pressure and temperature. An extensive variable doubles its value if the amount of matter in the system doubles, provided all the intensive variables remain the same. For example, the volume or total energy of the system doubles if we double the amount of matter in the system while holding the temperature and pressure of the system unchanged.

Summary

- A thermodynamic system, its boundary, and its surroundings must be defined with all the roles of the components fully explained before we can analyze a situation.
- Thermal equilibrium is reached with two objects if a third object is in thermal equilibrium with the other two separately.
- A general equation of state for a closed system has the form $f(p, V, T) = 0$, with an ideal gas as an illustrative example.

Conceptual Questions

Exercise:

Problem:

Consider these scenarios and state whether work is done by the system on the environment (SE) or by the environment on the system (ES): (a) opening a carbonated beverage; (b) filling a flat tire; (c) a sealed empty gas can expands on a hot day, bowing out the walls.

Solution:

a. SE; b. ES; c. ES

Problems

Exercise:**Problem:**

A gas follows $pV = bp + c_T$ on an isothermal curve, where p is the pressure, V is the volume, b is a constant, and c is a function of temperature. Show that a temperature scale under an isochoric process can be established with this gas and is identical to that of an ideal gas.

Solution:

$p(V - b) = -c_T$ is the temperature scale desired and mirrors the ideal gas if under constant volume.

Exercise:**Problem:**

A mole of gas has isobaric expansion coefficient $dV/dT = R/p$ and isochoric pressure-temperature coefficient $dp/dT = p/T$. Find the equation of state of the gas.

Exercise:**Problem:**

Find the equation of state of a solid that has an isobaric expansion coefficient $dV/dT = 2cT - bp$ and an isothermal pressure-volume coefficient $dV/dp = -bT$.

Solution:

$$V - bpT + cT^2 = 0$$

Glossary

boundary

imagined walls that separate the system and its surroundings

closed system

system that is mechanically and thermally isolated from its environment

environment
outside of the system being studied

equation of state
describes properties of matter under given physical conditions

equilibrium
thermal balance established between two objects or parts within a system

extensive variable
variable that is proportional to the amount of matter in the system

intensive variable
variable that is independent of the amount of matter in the system

open system
system that can exchange energy and/or matter with its surroundings

surroundings
environment that interacts with an open system

thermodynamic system
object and focus of thermodynamic study

Work, Heat, and Internal Energy

By the end of this section, you will be able to:

- Describe the work done by a system, heat transfer between objects, and internal energy change of a system
- Calculate the work, heat transfer, and internal energy change in a simple process

We discussed the concepts of work and energy earlier in mechanics. Examples and related issues of heat transfer between different objects have also been discussed in the preceding chapters. Here, we want to expand these concepts to a thermodynamic system and its environment. Specifically, we elaborated on the concepts of heat and heat transfer in the previous two chapters. Here, we want to understand how work is done by or to a thermodynamic system; how heat is transferred between a system and its environment; and how the total energy of the system changes under the influence of the work done and heat transfer.

Work Done by a System

A force created from any source can do work by moving an object through a displacement. Then how does a thermodynamic system do work? [\[link\]](#) shows a gas confined to a cylinder that has a movable piston at one end. If the gas expands against the piston, it exerts a force through a distance and does work on the piston. If the piston compresses the gas as it is moved inward, work is also done—in this case, on the gas. The work associated with such volume changes can be determined as follows: Let the gas pressure on the piston face be p . Then the force on the piston due to the gas is pA , where A is the area of the face. When the piston is pushed outward an infinitesimal distance dx , the magnitude of the work done by the gas is

Equation:

$$dW = F dx = pA dx.$$

Since the change in volume of the gas is $dV = A dx$, this becomes

Equation:

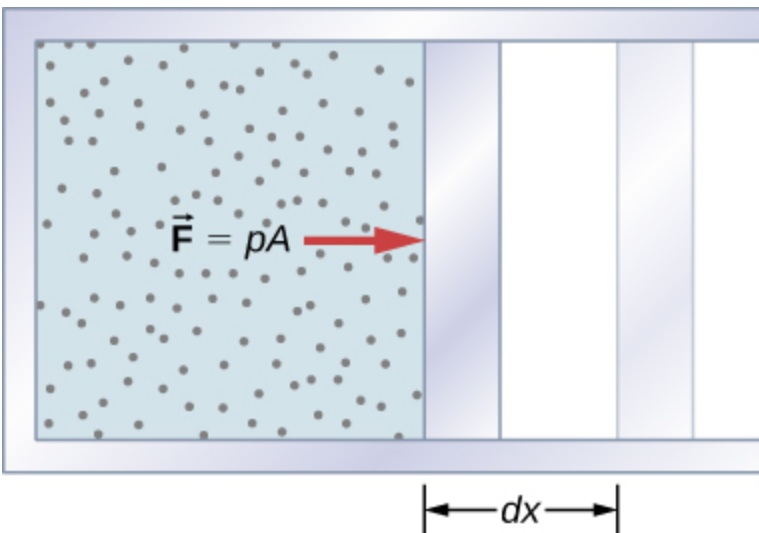
$$dW = pdV.$$

For a finite change in volume from V_1 to V_2 , we can integrate this equation from V_1 to V_2 to find the net work:

Note:

Equation:

$$W = \int_{V_1}^{V_2} pdV.$$

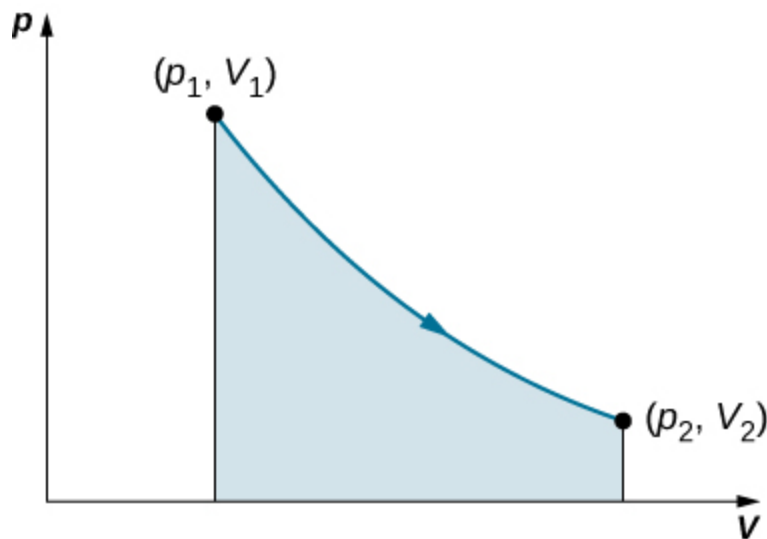


The work done by a confined gas in moving a piston a distance dx is given by

$$dW = Fdx = pdV.$$

This integral is only meaningful for a **quasi-static process**, which means a process that takes place in infinitesimally small steps, keeping the system at

thermal equilibrium. (We examine this idea in more detail later in this chapter.) Only then does a well-defined mathematical relationship (the equation of state) exist between the pressure and volume. This relationship can be plotted on a pV diagram of pressure versus volume, where the curve is the change of state. We can approximate such a process as one that occurs slowly, through a series of equilibrium states. The integral is interpreted graphically as the area under the pV curve (the shaded area of [link](#)). Work done by the gas is positive for expansion and negative for compression.

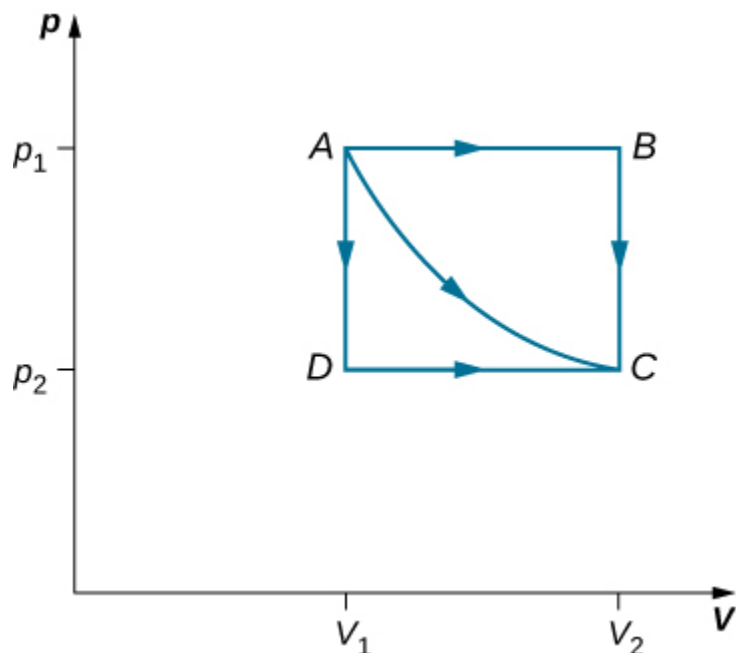


When a gas expands slowly from V_1 to V_2 , the work done by the system is represented by the shaded area under the pV curve.

Consider the two processes involving an ideal gas that are represented by paths AC and ABC in [link](#). The first process is an isothermal expansion, with the volume of the gas changing its volume from V_1 to V_2 . This isothermal process is represented by the curve between points A and C. The gas is kept at a constant temperature T by keeping it in thermal equilibrium with a heat reservoir at that temperature. From [link](#) and the ideal gas law,

Equation:

$$W = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \left(\frac{nRT}{V} \right) dV.$$



The paths ABC , AC , and ADC represent three different quasi-static transitions between the equilibrium states A and C .

The expansion is isothermal, so T remains constant over the entire process. Since n and R are also constant, the only variable in the integrand is V , so the work done by an ideal gas in an isothermal process is

Equation:

$$W = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \frac{V_2}{V_1}.$$

Notice that if $V_2 > V_1$ (expansion), W is positive, as expected.

The straight lines from A to B and then from B to C represent a different process. Here, a gas at a pressure p_1 first expands isobarically (constant pressure) and quasi-statically from V_1 to V_2 , after which it cools quasi-statically at the constant volume V_2 until its pressure drops to p_2 . From A to B , the pressure is constant at p , so the work over this part of the path is

Equation:

$$W = \int_{V_1}^{V_2} p dV = p_1 \int_{V_1}^{V_2} dV = p_1(V_2 - V_1).$$

From B to C , there is no change in volume and therefore no work is done. The net work over the path ABC is then

Equation:

$$W = p_1(V_2 - V_1) + 0 = p_1(V_2 - V_1).$$

A comparison of the expressions for the work done by the gas in the two processes of [\[link\]](#) shows that they are quite different. This illustrates a very important property of thermodynamic work: It is *path dependent*. We cannot determine the work done by a system as it goes from one equilibrium state to another unless we know its thermodynamic path. Different values of the work are associated with different paths.

Example:

Isothermal Expansion of a van der Waals Gas

Studies of a van der Waals gas require an adjustment to the ideal gas law that takes into consideration that gas molecules have a definite volume (see [The Kinetic Theory of Gases](#)). One mole of a van der Waals gas has an equation of state

Equation:

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT,$$

where a and b are two parameters for a specific gas. Suppose the gas expands isothermally and quasi-statically from volume V_1 to volume V_2 . How much work is done by the gas during the expansion?

Strategy

Because the equation of state is given, we can use [\[link\]](#) to express the pressure in terms of V and T . Furthermore, temperature T is a constant under the isothermal condition, so V becomes the only changing variable under the integral.

Solution

To evaluate this integral, we must express p as a function of V . From the given equation of state, the gas pressure is

Equation:

$$p = \frac{RT}{V - b} - \frac{a}{V^2}.$$

Because T is constant under the isothermal condition, the work done by 1 mol of a van der Waals gas in expanding from a volume V_1 to a volume V_2 is thus

Equation:

$$\begin{aligned} W &= \int_{V_1}^{V_2} \left(\frac{RT}{V - b} - \frac{a}{V^2} \right) dV = RT \ln(V - b) + \frac{a}{V} \Big|_{V_1}^{V_2} \\ &= RT \ln \left(\frac{V_2 - b}{V_1 - b} \right) + a \left(\frac{1}{V_2} - \frac{1}{V_1} \right). \end{aligned}$$

Significance

By taking into account the volume of molecules, the expression for work is much more complex. If, however, we set $a = 0$ and $b = 0$, we see that the expression for work matches exactly the work done by an isothermal process for one mole of an ideal gas.

Note:

Exercise:

Problem:

Check Your Understanding How much work is done by the gas, as given in [\[link\]](#), when it expands quasi-statically along the path *ADC*?

Solution:

$$p_2(V_2 - V_1)$$

Internal Energy

The **internal energy** E_{int} of a thermodynamic system is, by definition, the sum of the mechanical energies of all the molecules or entities in the system. If the kinetic and potential energies of molecule i are K_i and U_i , respectively, then the internal energy of the system is the average of the total mechanical energy of all the entities:

Note:

Equation:

$$E_{\text{int}} = \sum_i (\bar{K}_i + \bar{U}_i),$$

where the summation is over all the molecules of the system, and the bars over K and U indicate average values. The kinetic energy K_i of an individual molecule includes contributions due to its rotation and vibration, as well as its translational energy $m_i v_i^2/2$, where v_i is the molecule's speed measured relative to the center of mass of the system. The potential energy

U_i is associated only with the interactions between molecule i and the other molecules of the system. In fact, neither the system's location nor its motion is of any consequence as far as the internal energy is concerned. The internal energy of the system is not affected by moving it from the basement to the roof of a 100-story building or by placing it on a moving train.

In an ideal monatomic gas, each molecule is a single atom. Consequently, there is no rotational or vibrational kinetic energy and $K_i = m_i v_i^2 / 2$. Furthermore, there are no interatomic interactions (collisions notwithstanding), so $U_i = \text{constant}$, which we set to zero. The internal energy is therefore due to translational kinetic energy only and

Equation:

$$E_{\text{int}} = \sum_i \bar{K}_i = \sum_i \frac{1}{2} m_i v_i^2.$$

From the discussion in the preceding chapter, we know that the average kinetic energy of a molecule in an ideal monatomic gas is

Equation:

$$\frac{1}{2} m_i \bar{v}_i^2 = \frac{3}{2} k_B T,$$

where T is the Kelvin temperature of the gas. Consequently, the average mechanical energy per molecule of an ideal monatomic gas is also $3k_B T / 2$, that is,

Equation:

$$K_i + U_i = \bar{K}_i = \frac{3}{2} k_B T.$$

The internal energy is just the number of molecules multiplied by the average mechanical energy per molecule. Thus for n moles of an ideal monatomic gas,

Note:

Equation:

$$E_{\text{int}} = nN_A \left(\frac{3}{2} k_B T \right) = \frac{3}{2} nRT.$$

Notice that the internal energy of a given quantity of an ideal monatomic gas depends on just the temperature and is completely independent of the pressure and volume of the gas. For other systems, the internal energy cannot be expressed so simply. However, an increase in internal energy can often be associated with an increase in temperature.

We know from the zeroth law of thermodynamics that when two systems are placed in thermal contact, they eventually reach thermal equilibrium, at which point they are at the same temperature. As an example, suppose we mix two monatomic ideal gases. Now, the energy per molecule of an ideal monatomic gas is proportional to its temperature. Thus, when the two gases are mixed, the molecules of the hotter gas must lose energy and the molecules of the colder gas must gain energy. This continues until thermal equilibrium is reached, at which point, the temperature, and therefore the average translational kinetic energy per molecule, is the same for both gases. The approach to equilibrium for real systems is somewhat more complicated than for an ideal monatomic gas. Nevertheless, we can still say that energy is exchanged between the systems until their temperatures are the same.

Summary

- Positive (negative) work is done by a thermodynamic system when it expands (contracts) under an external pressure.
- Heat is the energy transferred between two objects (or two parts of a system) because of a temperature difference.
- Internal energy of a thermodynamic system is its total mechanical energy.

Conceptual Questions

Exercise:

Problem:

Is it possible to determine whether a change in internal energy is caused by heat transferred, by work performed, or by a combination of the two?

Exercise:

Problem:

When a liquid is vaporized, its change in internal energy is not equal to the heat added. Why?

Solution:

Some of the energy goes into changing the phase of the liquid to gas.

Exercise:

Problem:

Why does a bicycle pump feel warm as you inflate your tire?

Exercise:

Problem:

Is it possible for the temperature of a system to remain constant when heat flows into or out of it? If so, give examples.

Solution:

Yes, as long as the work done equals the heat added there will be no change in internal energy and thereby no change in temperature. When water freezes or when ice melts while removing or adding heat, respectively, the temperature remains constant.

Problems

Exercise:

Problem:

A gas at a pressure of 2.00 atm undergoes a quasi-static isobaric expansion from 3.00 to 5.00 L. How much work is done by the gas?

Exercise:

Problem:

It takes 500 J of work to compress quasi-statically 0.50 mol of an ideal gas to one-fifth its original volume. Calculate the temperature of the gas, assuming it remains constant during the compression.

Solution:

74 K

Exercise:

Problem:

It is found that, when a dilute gas expands quasi-statically from 0.50 to 4.0 L, it does 250 J of work. Assuming that the gas temperature remains constant at 300 K, how many moles of gas are present?

Exercise:

Problem:

In a quasi-static isobaric expansion, 500 J of work are done by the gas. If the gas pressure is 0.80 atm, what is the fractional increase in the volume of the gas, assuming it was originally at 20.0 L?

Solution:

1.4 times

Exercise:

Problem:

When a gas undergoes a quasi-static isobaric change in volume from 10.0 to 2.0 L, 15 J of work from an external source are required. What is the pressure of the gas?

Exercise:**Problem:**

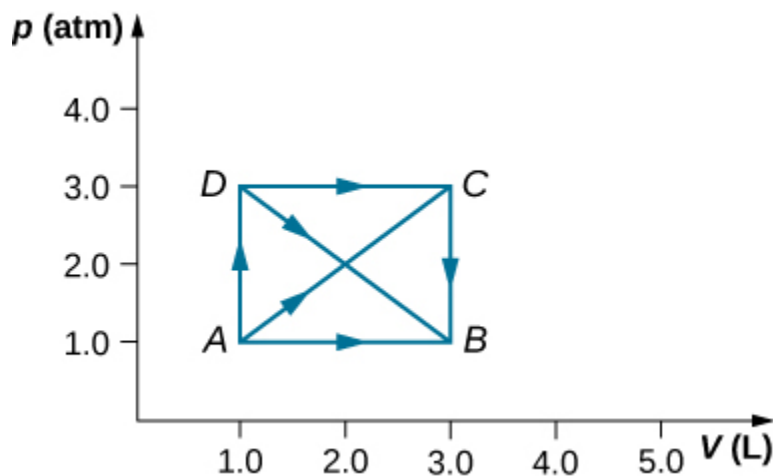
An ideal gas expands quasi-statically and isothermally from a state with pressure p and volume V to a state with volume $4V$. Show that the work done by the gas in the expansion is $pV(\ln 4)$.

Solution:

$$pV\ln(4)$$

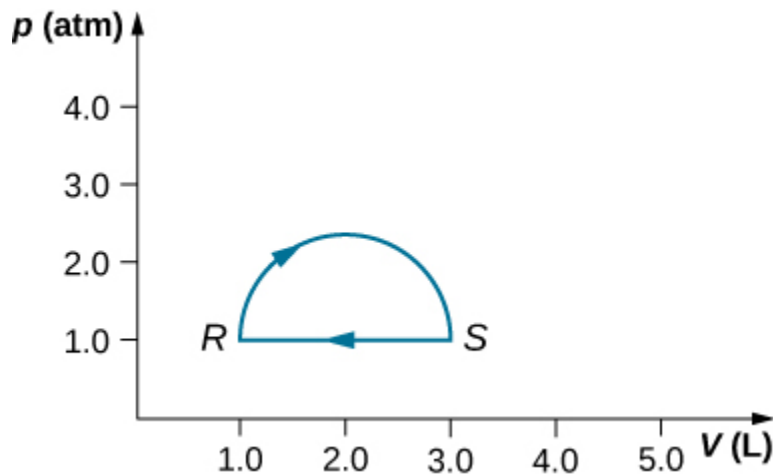
Exercise:**Problem:**

As shown below, calculate the work done by the gas in the quasi-static processes represented by the paths (a) AB; (b) ADB; (c) ACB; and (d) ADCB.

**Exercise:**

Problem:

(a) Calculate the work done by the gas along the closed path shown below. The curved section between R and S is semicircular. (b) If the process is carried out in the opposite direction, what is the work done by the gas?



Solution:

a. 160 J; b. -160 J

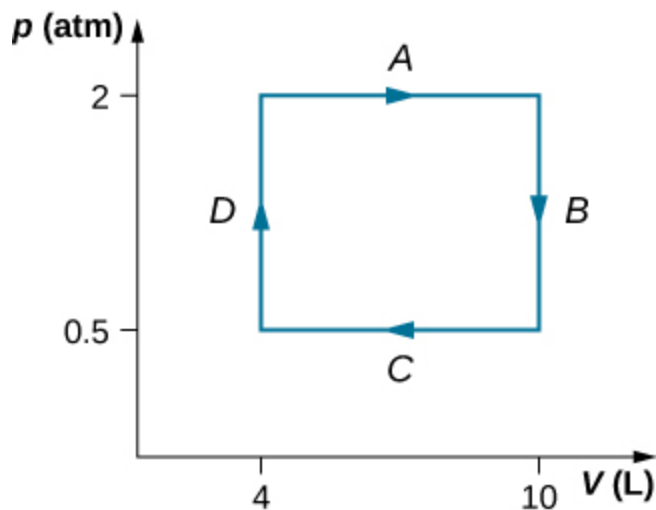
Exercise:**Problem:**

An ideal gas expands quasi-statically to three times its original volume. Which process requires more work from the gas, an isothermal process or an isobaric one? Determine the ratio of the work done in these processes.

Exercise:

Problem:

A dilute gas at a pressure of 2.0 atm and a volume of 4.0 L is taken through the following quasi-static steps: (a) an isobaric expansion to a volume of 10.0 L, (b) an isochoric change to a pressure of 0.50 atm, (c) an isobaric compression to a volume of 4.0 L, and (d) an isochoric change to a pressure of 2.0 atm. Show these steps on a pV diagram and determine from your graph the net work done by the gas.

Solution:

$$W = 900 \text{ J}$$

Exercise:**Problem:**

What is the average mechanical energy of the atoms of an ideal monatomic gas at 300 K?

Exercise:

Problem:

What is the internal energy of 6.00 mol of an ideal monatomic gas at 200 °C ?

Solution:

$$3.53 \times 10^4 \text{ J}$$

Exercise:**Problem:**

Calculate the internal energy of 15 mg of helium at a temperature of 0 °C.

Exercise:**Problem:**

Two monatomic ideal gases A and B are at the same temperature. If 1.0 g of gas A has the same internal energy as 0.10 g of gas B, what are (a) the ratio of the number of moles of each gas and (b) the ratio of the atomic masses of the two gases?

Solution:

a. 1:1; b. 10:1

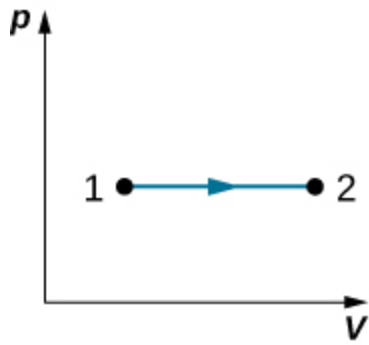
Exercise:**Problem:**

The van der Waals coefficients for oxygen are $a = 0.138 \text{ J} \cdot \text{m}^3/\text{mol}^2$ and $b = 3.18 \times 10^{-5} \text{ m}^3/\text{mol}$. Use these values to draw a van der Waals isotherm of oxygen at 100 K. On the same graph, draw isotherms of one mole of an ideal gas.

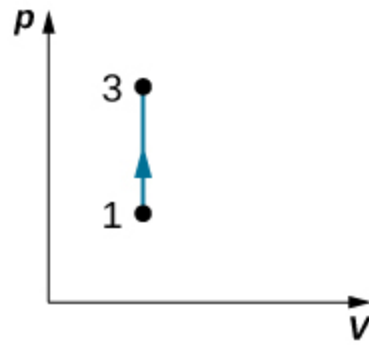
Exercise:

Problem:

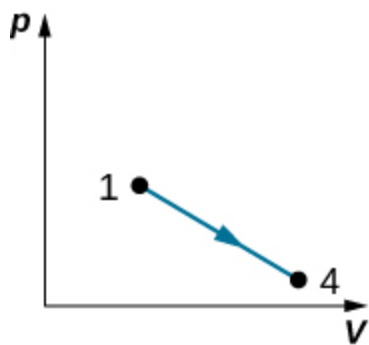
Find the work done in the quasi-static processes shown below. The states are given as (p, V) values for the points in the pV plane: 1 (3 atm, 4 L), 2 (3 atm, 6 L), 3 (5 atm, 4 L), 4 (2 atm, 6 L), 5 (4 atm, 2 L), 6 (5 atm, 5 L), and 7 (2 atm, 5 L).



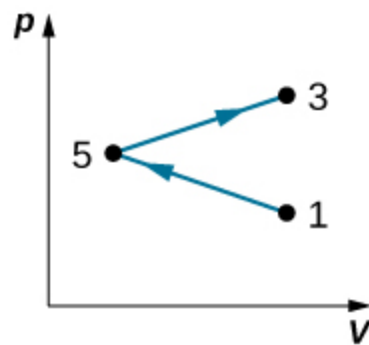
(a)



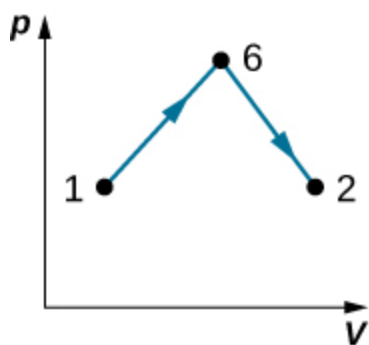
(b)



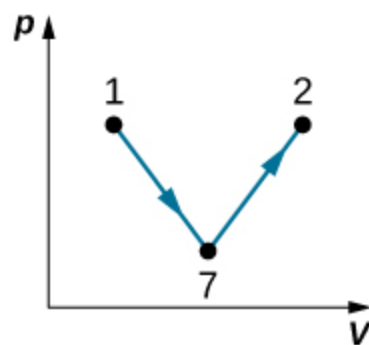
(c)



(d)



(e)



(f)

Solution:

a. 600 J; b. 0; c. 500 J; d. 200 J; e. 800 J; f. 500 J

Glossary

internal energy

average of the total mechanical energy of all the molecules or entities in the system

quasi-static process

evolution of a system that goes so slowly that the system involved is always in thermodynamic equilibrium

First Law of Thermodynamics

By the end of this section, you will be able to:

- State the first law of thermodynamics and explain how it is applied
- Explain how heat transfer, work done, and internal energy change are related in any thermodynamic process

Now that we have seen how to calculate internal energy, heat, and work done for a thermodynamic system undergoing change during some process, we can see how these quantities interact to affect the amount of change that can occur. This interaction is given by the first law of thermodynamics. British scientist and novelist C. P. Snow (1905–1980) is credited with a joke about the four laws of thermodynamics. His humorous statement of the first law of thermodynamics is stated “you can’t win,” or in other words, you cannot get more energy out of a system than you put into it. We will see in this chapter how internal energy, heat, and work all play a role in the first law of thermodynamics.

Suppose Q represents the heat exchanged between a system and the environment, and W is the work done by or on the system. The first law states that the change in internal energy of that system is given by $Q - W$. Since added heat increases the internal energy of a system, Q is positive when it is added to the system and negative when it is removed from the system.

When a gas expands, it does work and its internal energy decreases. Thus, W is positive when work is done by the system and negative when work is done on the system. This sign convention is summarized in [\[link\]](#). The **first law of thermodynamics** is stated as follows:

Note:

First Law of Thermodynamics

Associated with every equilibrium state of a system is its internal energy E_{int} . The change in E_{int} for any transition between two equilibrium states is

Equation:

$$\Delta E_{\text{int}} = Q - W$$

where Q and W represent, respectively, the heat exchanged by the system and the work done by or on the system.

Thermodynamic Sign Conventions for Heat and Work	
Process	Convention
Heat added to system	$Q > 0$
Heat removed from system	$Q < 0$
Work done by system	$W > 0$
Work done on system	$W < 0$

The first law is a statement of energy conservation. It tells us that a system can exchange energy with its surroundings by the transmission of heat and by the performance of work. The net energy exchanged is then equal to the change in the total mechanical energy of the molecules of the system (i.e., the system's internal energy). Thus, if a system is isolated, its internal energy must remain constant.

Although Q and W both depend on the thermodynamic path taken between two equilibrium states, their difference $Q - W$ does not. [\[link\]](#) shows the pV diagram of a system that is making the transition from A to B repeatedly along different thermodynamic paths. Along path 1, the system absorbs heat Q_1 and does work W_1 ; along path 2, it absorbs heat Q_2 and does work W_2 , and so on. The values of Q_i and W_i may vary from path to path, but we have **Equation:**

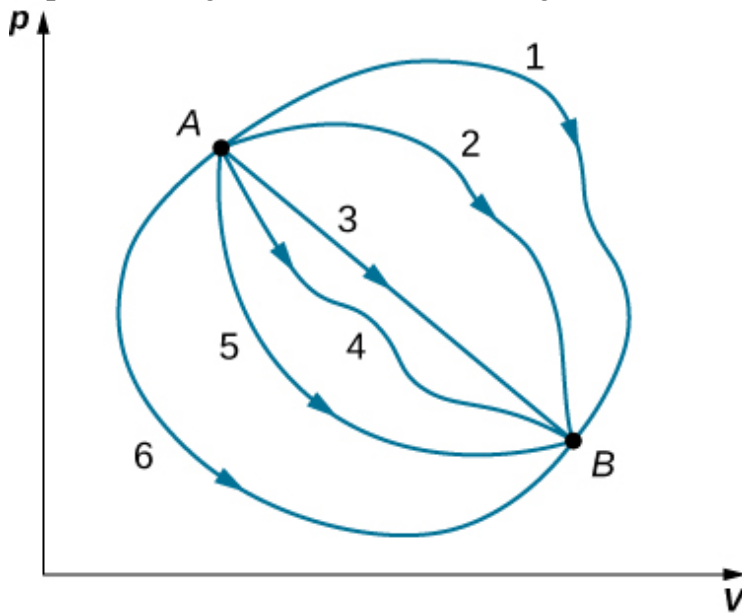
$$Q_1 - W_1 = Q_2 - W_2 = \cdots = Q_i - W_i = \cdots,$$

or

Equation:

$$\Delta E_{\text{int}1} = \Delta E_{\text{int}2} = \dots = \Delta E_{\text{int}i} = \dots$$

That is, the change in the internal energy of the system between A and B is path independent. In the chapter on potential energy and the conservation of energy, we encountered another path-independent quantity: the change in potential energy between two arbitrary points in space. This change represents the negative of the work done by a conservative force between the two points. The potential energy is a function of spatial coordinates, whereas the internal energy is a function of thermodynamic variables. For example, we might write $E_{\text{int}}(T, p)$ for the internal energy. Functions such as internal energy and potential energy are known as *state functions* because their values depend solely on the state of the system.



Different thermodynamic paths taken by a system in going from state A to state B .

For all transitions, the change in the internal energy of the system

$$\Delta E_{\text{int}} = Q - W \text{ is the same.}$$

Often the first law is used in its differential form, which is

Equation:

$$dE_{\text{int}} = dQ - dW.$$

Here dE_{int} is an infinitesimal change in internal energy when an infinitesimal amount of heat dQ is exchanged with the system and an infinitesimal amount of work dW is done by (positive in sign) or on (negative in sign) the system.

Example:

Changes of State and the First Law

During a thermodynamic process, a system moves from state A to state B , it is supplied with 400 J of heat and does 100 J of work. (a) For this transition, what is the system's change in internal energy? (b) If the system then moves from state B back to state A , what is its change in internal energy? (c) If in moving from A to B along a different path, $W'_{AB} = 400$ J of work is done on the system, how much heat does it absorb?

Strategy

The first law of thermodynamics relates the internal energy change, work done by the system, and the heat transferred to the system in a simple equation. The internal energy is a function of state and is therefore fixed at any given point regardless of how the system reaches the state.

Solution

- a. From the first law, the change in the system's internal energy is

Equation:

$$\Delta E_{\text{int}AB} = Q_{AB} - W_{AB} = 400 \text{ J} - 100 \text{ J} = 300 \text{ J}.$$

- b. Consider a closed path that passes through the states A and B . Internal energy is a state function, so ΔE_{int} is zero for a closed path. Thus

Equation:

$$\Delta E_{\text{int}} = \Delta E_{\text{int}AB} + \Delta E_{\text{int}BA} = 0,$$

and

Equation:

$$\Delta E_{\text{int}AB} = -\Delta E_{\text{int}BA}.$$

This yields

Equation:

$$\Delta E_{\text{int}BA} = -300 \text{ J}.$$

c. The change in internal energy is the same for any path, so

Equation:

$$\begin{aligned}\Delta E_{\text{int}AB} &= \Delta E'_{\text{int}AB} = Q'_{AB} - W'_{AB}; \\ 300 \text{ J} &= Q'_{AB} - (-400 \text{ J}),\end{aligned}$$

and the heat exchanged is

Equation:

$$Q'_{AB} = -100 \text{ J}.$$

The negative sign indicates that the system loses heat in this transition.

Significance

When a closed cycle is considered for the first law of thermodynamics, the change in internal energy around the whole path is equal to zero. If friction were to play a role in this example, less work would result from this heat added. [\[link\]](#) takes into consideration what happens if friction plays a role.

Notice that in [\[link\]](#), we did not assume that the transitions were quasi-static. This is because the first law is not subject to such a restriction. It describes transitions between equilibrium states but is not concerned with the intermediate states. The system does not have to pass through only

equilibrium states. For example, if a gas in a steel container at a well-defined temperature and pressure is made to explode by means of a spark, some of the gas may condense, different gas molecules may combine to form new compounds, and there may be all sorts of turbulence in the container—but eventually, the system will settle down to a new equilibrium state. This system is clearly not in equilibrium during its transition; however, its behavior is still governed by the first law because the process starts and ends with the system in equilibrium states.

Example:**Polishing a Fitting**

A machinist polishes a 0.50-kg copper fitting with a piece of emery cloth for 2.0 min. He moves the cloth across the fitting at a constant speed of 1.0 m/s by applying a force of 20 N, tangent to the surface of the fitting. (a) What is the total work done on the fitting by the machinist? (b) What is the increase in the internal energy of the fitting? Assume that the change in the internal energy of the cloth is negligible and that no heat is exchanged between the fitting and its environment. (c) What is the increase in the temperature of the fitting?

Strategy

The machinist's force over a distance that can be calculated from the speed and time given is the work done on the system. The work, in turn, increases the internal energy of the system. This energy can be interpreted as the heat that raises the temperature of the system via its heat capacity. Be careful with the sign of each quantity.

Solution

- a. The power created by a force on an object or the rate at which the machinist does frictional work on the fitting is $\vec{\mathbf{F}} \cdot \vec{\mathbf{v}} = -Fv$. Thus, in an elapsed time Δt (2.0 min), the work done on the fitting is

Equation:

$$\begin{aligned} W &= -Fv\Delta t = -(20 \text{ N})(0.1 \text{ m/s})(1.2 \times 10^2 \text{ s}) \\ &= -2.4 \times 10^3 \text{ J.} \end{aligned}$$

- b. By assumption, no heat is exchanged between the fitting and its environment, so the first law gives for the change in the internal energy of the fitting:

Equation:

$$\Delta E_{\text{int}} = -W = 2.4 \times 10^3 \text{ J}.$$

- c. Since ΔE_{int} is path independent, the effect of the $2.4 \times 10^3 \text{ J}$ of work is the same as if it were supplied at atmospheric pressure by a transfer of heat. Thus,

Equation:

$$2.4 \times 10^3 \text{ J} = mc\Delta T = (0.50 \text{ kg})(3.9 \times 10^2 \text{ J/kg} \cdot ^\circ\text{C})\Delta T,$$

and the increase in the temperature of the fitting is

Equation:

$$\Delta T = 12 ^\circ\text{C},$$

where we have used the value for the specific heat of copper,
 $c = 3.9 \times 10^2 \text{ J/kg} \cdot ^\circ\text{C}$.

Significance

If heat were released, the change in internal energy would be less and cause less of a temperature change than what was calculated in the problem.

Note:

Exercise:

Problem:

Check Your Understanding The quantities below represent four different transitions between the same initial and final state. Fill in the blanks.

$Q \text{ (J)}$	$W \text{ (J)}$	$\Delta E_{\text{int}} \text{ (J)}$
-80	-120	
90		
	40	
	-40	

Solution:

Line 1, $\Delta E_{\text{int}} = 40 \text{ J}$; line 2, $W = 50 \text{ J}$ and $\Delta E_{\text{int}} = 40 \text{ J}$; line 3, $Q = 80 \text{ J}$ and $\Delta E_{\text{int}} = 40 \text{ J}$; and line 4, $Q = 0$ and $\Delta E_{\text{int}} = 40 \text{ J}$

Example:

An Ideal Gas Making Transitions between Two States

Consider the quasi-static expansions of an ideal gas between the equilibrium states A and C of [\[link\]](#). If 515 J of heat are added to the gas as it traverses the path ABC , how much heat is required for the transition along ADC ?

Assume that

$p_1 = 2.10 \times 10^5 \text{ N/m}^2$, $p_2 = 1.05 \times 10^5 \text{ N/m}^2$, $V_1 = 2.25 \times 10^{-3} \text{ m}^3$, and $V_2 = 4.50 \times 10^{-3} \text{ m}^3$.

Strategy

The difference in work done between process ABC and process ADC is the area enclosed by $ABCD$. Because the change of the internal energy (a function of state) is the same for both processes, the difference in work is thus the same as the difference in heat transferred to the system.

Solution

For path ABC , the heat added is $Q_{ABC} = 515 \text{ J}$ and the work done by the gas is the area under the path on the pV diagram, which is

Equation:

$$W_{ABC} = p_1(V_2 - V_1) = 473 \text{ J.}$$

Along ADC , the work done by the gas is again the area under the path:

Equation:

$$W_{ADC} = p_2(V_2 - V_1) = 236 \text{ J.}$$

Then using the strategy we just described, we have

Equation:

$$Q_{ADC} - Q_{ABC} = W_{ADC} - W_{ABC},$$

which leads to

Equation:

$$Q_{ADC} = Q_{ABC} + W_{ADC} - W_{ABC} = (515 + 236 - 473) \text{ J} = 278 \text{ J.}$$

Significance

The work calculations in this problem are made simple since no work is done along AD and BC and along AB and DC ; the pressure is constant over the volume change, so the work done is simply $p\Delta V$. An isothermal line could also have been used, as we have derived the work for an isothermal process as $W = nRT \ln \frac{V_2}{V_1}$.

Example:

Isothermal Expansion of an Ideal Gas

Heat is added to 1 mol of an ideal monatomic gas confined to a cylinder with a movable piston at one end. The gas expands quasi-statically at a constant temperature of 300 K until its volume increases from V to $3V$. (a) What is the change in internal energy of the gas? (b) How much work does the gas do? (c) How much heat is added to the gas?

Strategy

(a) Because the system is an ideal gas, the internal energy only changes when the temperature changes. (b) The heat added to the system is therefore purely used to do work that has been calculated in [Work, Heat, and Internal Energy](#). (c) Lastly, the first law of thermodynamics can be used to calculate the heat added to the gas.

Solution

- a. We saw in the preceding section that the internal energy of an ideal monatomic gas is a function only of temperature. Since $\Delta T = 0$, for this process, $\Delta E_{\text{int}} = 0$.
- b. The quasi-static isothermal expansion of an ideal gas was considered in the preceding section and was found to be

Equation:

$$\begin{aligned} W &= nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{3V}{V} \\ &= (1.00 \text{ mol})(8.314 \text{ J/K} \cdot \text{mol})(300 \text{ K})(\ln 3) = 2.74 \times 10^3 \text{ J}. \end{aligned}$$

- c. With the results of parts (a) and (b), we can use the first law to determine the heat added:

Equation:

$$\Delta E_{\text{int}} = Q - W = 0,$$

which leads to

Equation:

$$Q = W = 2.74 \times 10^3 \text{ J}.$$

Significance

An isothermal process has no change in the internal energy. Based on that, the first law of thermodynamics reduces to $Q = W$.

Note:

Exercise:

Problem:

Check Your Understanding Why was it necessary to state that the process of [\[link\]](#) is quasi-static?

Solution:

So that the process is represented by the curve $p = nRT/V$ on the pV plot for the evaluation of work.

Example:**Vaporizing Water**

When 1.00 g of water at 100 °C changes from the liquid to the gas phase at atmospheric pressure, its change in volume is $1.67 \times 10^{-3} \text{ m}^3$. (a) How much heat must be added to vaporize the water? (b) How much work is done by the water against the atmosphere in its expansion? (c) What is the change in the internal energy of the water?

Strategy

We can first figure out how much heat is needed from the latent heat of vaporization of the water. From the volume change, we can calculate the work done from $W = p\Delta V$ because the pressure is constant. Then, the first law of thermodynamics provides us with the change in the internal energy.

Solution

- a. With L_v representing the latent heat of vaporization, the heat required to vaporize the water is

Equation:

$$Q = mL_v = (1.00 \text{ g})(2.26 \times 10^3 \text{ J/g}) = 2.26 \times 10^3 \text{ J}.$$

- b. Since the pressure on the system is constant at $1.00 \text{ atm} = 1.01 \times 10^5 \text{ N/m}^2$, the work done by the water as it is vaporized is

Equation:

$$W = p\Delta V = (1.01 \times 10^5 \text{ N/m}^2)(1.67 \times 10^{-3} \text{ m}^3) = 169 \text{ J}.$$

- c. From the first law, the thermal energy of the water during its vaporization changes by

Equation:

$$\Delta E_{\text{int}} = Q - W = 2.26 \times 10^3 \text{ J} - 169 \text{ J} = 2.09 \times 10^3 \text{ J}.$$

Significance

We note that in part (c), we see a change in internal energy, yet there is no change in temperature. Ideal gases that are not undergoing phase changes have the internal energy proportional to temperature. Internal energy in general is the sum of all energy in the system.

Note:**Exercise:****Problem:**

Check Your Understanding When 1.00 g of ammonia boils at atmospheric pressure and -33.0°C , its volume changes from 1.47 to 1130 cm^3 . Its heat of vaporization at this pressure is $1.37 \times 10^6 \text{ J/kg}$. What is the change in the internal energy of the ammonia when it vaporizes?

Solution:

$$1.26 \times 10^3 \text{ J}.$$

Note:

View this [site](#) to learn about how the first law of thermodynamics. First, pump some heavy species molecules into the chamber. Then, play around by doing work (pushing the wall to the right where the person is located) to see how the internal energy changes (as seen by temperature). Then, look at how heat added changes the internal energy. Finally, you can set a parameter constant such as temperature and see what happens when you do work to keep the temperature constant (*Note:* You might see a change in these variables initially if you are moving around quickly in the simulation, but ultimately, this value will return to its equilibrium value).

Summary

- The internal energy of a thermodynamic system is a function of state and thus is unique for every equilibrium state of the system.
- The increase in the internal energy of the thermodynamic system is given by the heat added to the system less the work done by the system in any thermodynamics process.

Conceptual Questions

Exercise:

Problem:

What does the first law of thermodynamics tell us about the energy of the universe?

Exercise:

Problem:

Does adding heat to a system always increase its internal energy?

Solution:

If more work is done on the system than heat added, the internal energy of the system will actually decrease.

Exercise:

Problem:

A great deal of effort, time, and money has been spent in the quest for a so-called perpetual-motion machine, which is defined as a hypothetical machine that operates or produces useful work indefinitely and/or a hypothetical machine that produces more work or energy than it consumes. Explain, in terms of the first law of thermodynamics, why or why not such a machine is likely to be constructed.

Problems

Exercise:**Problem:**

When a dilute gas expands quasi-statically from 0.50 to 4.0 L, it does 250 J of work. Assuming that the gas temperature remains constant at 300 K, (a) what is the change in the internal energy of the gas? (b) How much heat is absorbed by the gas in this process?

Exercise:**Problem:**

In a quasi-static isobaric expansion, 500 J of work are done by the gas. The gas pressure is 0.80 atm and it was originally at 20.0 L. If the internal energy of the gas increased by 80 J in the expansion, how much heat does the gas absorb?

Solution:

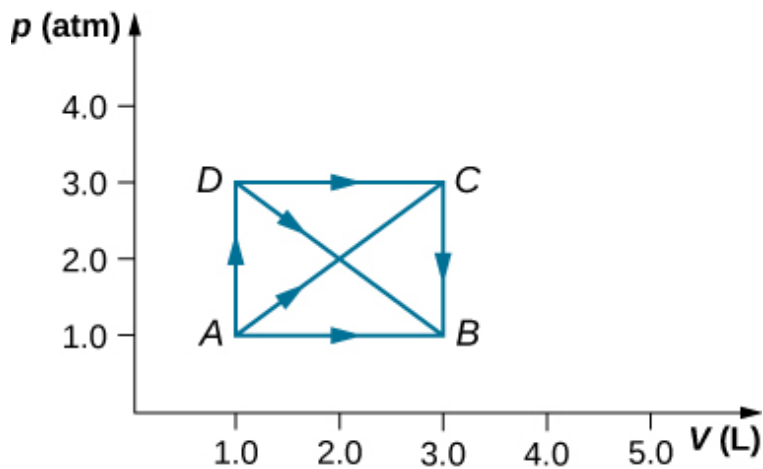
580 J

Exercise:**Problem:**

An ideal gas expands quasi-statically and isothermally from a state with pressure p and volume V to a state with volume $4V$. How much heat is added to the expanding gas?

Exercise:**Problem:**

As shown below, if the heat absorbed by the gas along AB is 400 J, determine the quantities of heat absorbed along (a) ADB; (b) ACB; and (c) ADCB.



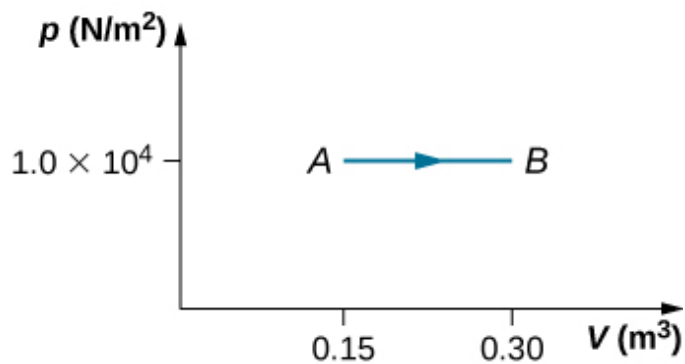
Solution:

a. 600 J; b. 600 J; c. 800 J

Exercise:

Problem:

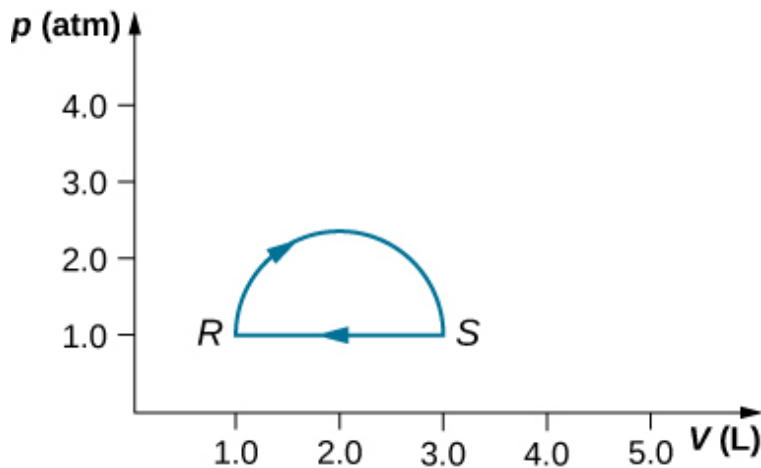
During the isobaric expansion from A to B represented below, 130 J of heat are removed from the gas. What is the change in its internal energy?



Exercise:

Problem:

(a) What is the change in internal energy for the process represented by the closed path shown below? (b) How much heat is exchanged? (c) If the path is traversed in the opposite direction, how much heat is exchanged?

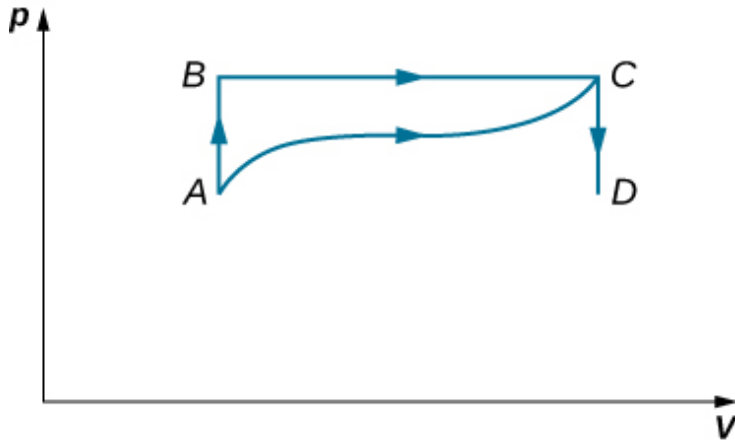


Solution:

a. 0; b. 160 J; c. -160 J

Exercise:**Problem:**

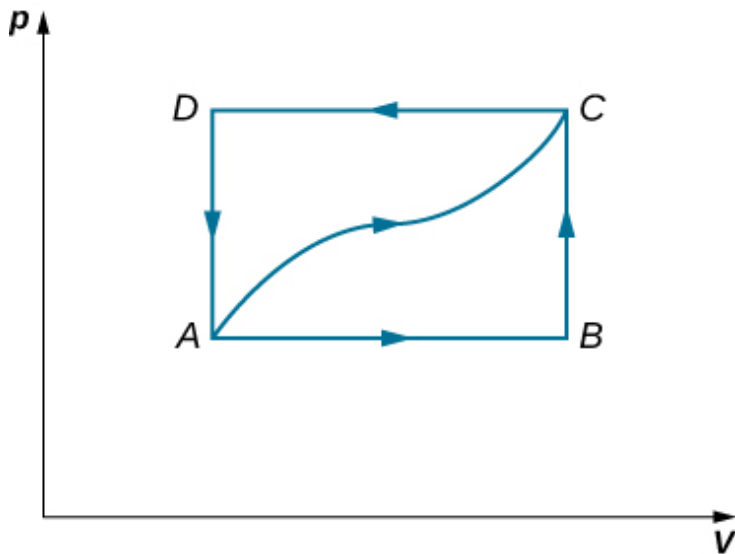
When a gas expands along path AC shown below, it does 400 J of work and absorbs either 200 or 400 J of heat. (a) Suppose you are told that along path ABC, the gas absorbs either 200 or 400 J of heat. Which of these values is correct? (b) Give the correct answer from part (a), how much work is done by the gas along ABC? (c) Along CD, the internal energy of the gas decreases by 50 J. How much heat is exchanged by the gas along this path?



Exercise:

Problem:

When a gas expands along AB (see below), it does 500 J of work and absorbs 250 J of heat. When the gas expands along AC , it does 700 J of work and absorbs 300 J of heat. (a) How much heat does the gas exchange along BC ? (b) When the gas makes the transmission from C to A along CDA , 800 J of work are done on it from C to D . How much heat does it exchange along CDA ?



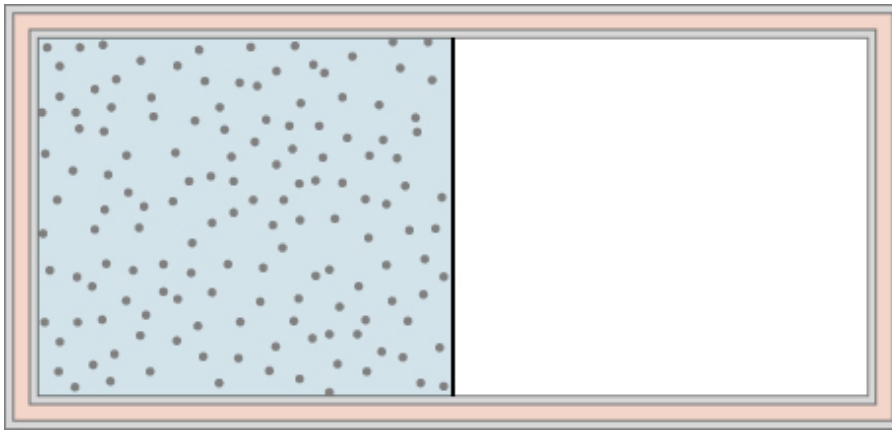
Solution:

a. -150 J ; b. -400 J

Exercise:

Problem:

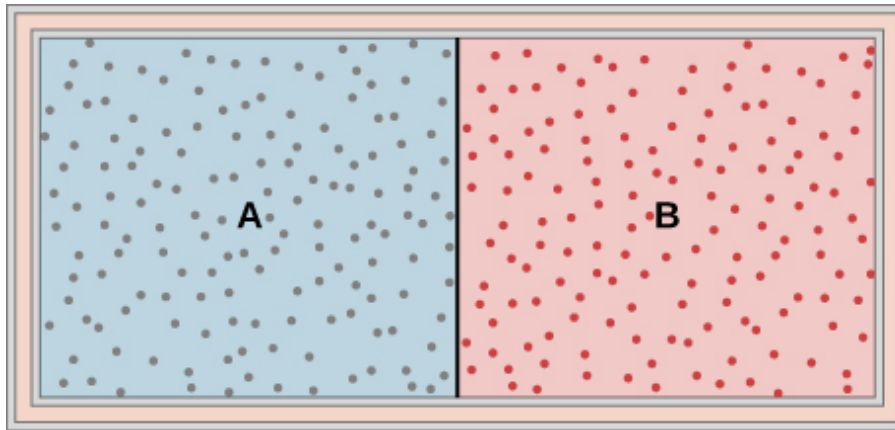
A dilute gas is stored in the left chamber of a container whose walls are perfectly insulating (see below), and the right chamber is evacuated. When the partition is removed, the gas expands and fills the entire container. Calculate the work done by the gas. Does the internal energy of the gas change in this process?



Exercise:

Problem:

Ideal gases A and B are stored in the left and right chambers of an insulated container, as shown below. The partition is removed and the gases mix. Is any work done in this process? If the temperatures of A and B are initially equal, what happens to their common temperature after they are mixed?



Solution:

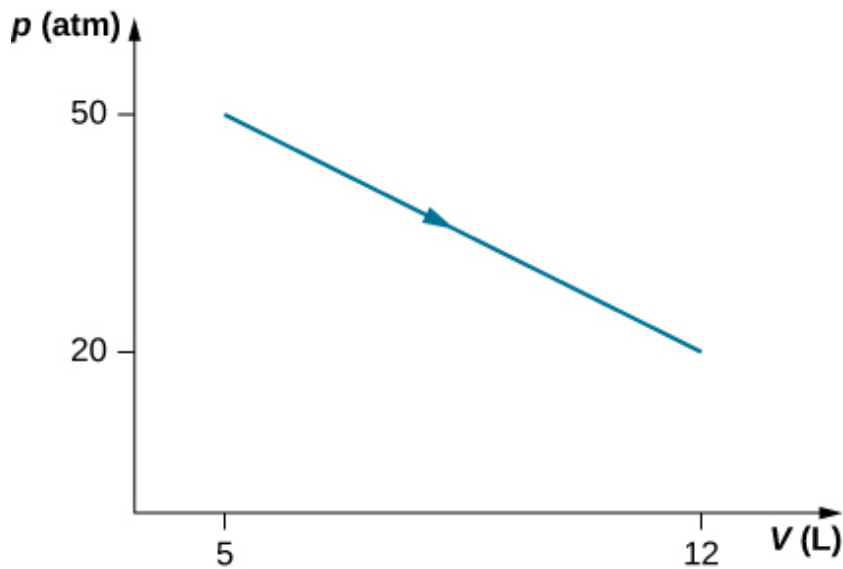
No work is done and they reach the same common temperature.

Exercise:**Problem:**

An ideal monatomic gas at a pressure of $2.0 \times 10^5 \text{ N/m}^2$ and a temperature of 300 K undergoes a quasi-static isobaric expansion from 2.0×10^3 to $4.0 \times 10^3 \text{ cm}^3$. (a) What is the work done by the gas? (b) What is the temperature of the gas after the expansion? (c) How many moles of gas are there? (d) What is the change in internal energy of the gas? (e) How much heat is added to the gas?

Exercise:**Problem:**

Consider the process for steam in a cylinder shown below. Suppose the change in the internal energy in this process is 30 kJ. Find the heat entering the system.



Solution:

54,500 J

Exercise:

Problem:

The state of 30 moles of steam in a cylinder is changed in a cyclic manner from a-b-c-a, where the pressure and volume of the states are: a (30 atm, 20 L), b (50 atm, 20 L), and c (50 atm, 45 L). Assume each change takes place along the line connecting the initial and final states in the pV plane. (a) Display the cycle in the pV plane. (b) Find the net work done by the steam in one cycle. (c) Find the net amount of heat flow in the steam over the course of one cycle.

Exercise:

Problem:

A monatomic ideal gas undergoes a quasi-static process that is described by the function $p(V) = p_1 + 3(V - V_1)$, where the starting state is (p_1, V_1) and the final state (p_2, V_2) . Assume the system consists of n moles of the gas in a container that can exchange heat with the environment and whose volume can change freely. (a) Evaluate the work done by the gas during the change in the state. (b) Find the change in internal energy of the gas. (c) Find the heat input to the gas during the change. (d) What are initial and final temperatures?

Solution:

a. $(p_1 + 3V_1^2)(V_2 - V_1) - 3V_1(V_2^2 - V_1^2) + (V_2^3 - V_1^3)$; b. $\frac{3}{2}(p_2V_2 - p_1V_1)$; c. the sum of parts (a) and (b); d. $T_1 = \frac{p_1V_1}{nR}$ and $T_2 = \frac{p_2V_2}{nR}$

Exercise:**Problem:**

A metallic container of fixed volume of $2.5 \times 10^{-3} \text{ m}^3$ immersed in a large tank of temperature 27°C contains two compartments separated by a freely movable wall. Initially, the wall is kept in place by a stopper so that there are 0.02 mol of the nitrogen gas on one side and 0.03 mol of the oxygen gas on the other side, each occupying half the volume. When the stopper is removed, the wall moves and comes to a final position. The movement of the wall is controlled so that the wall moves in infinitesimal quasi-static steps. (a) Find the final volumes of the two sides assuming the ideal gas behavior for the two gases. (b) How much work does each gas do on the other? (c) What is the change in the internal energy of each gas? (d) Find the amount of heat that enters or leaves each gas.

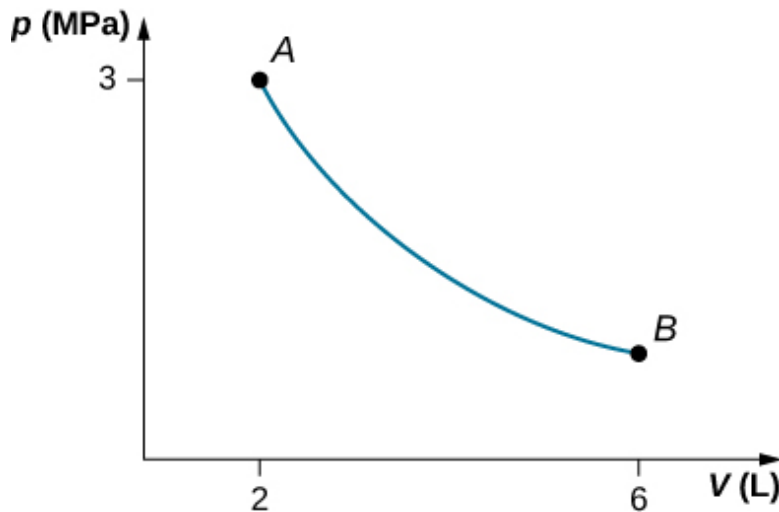
Exercise:

Problem:

A gas in a cylindrical closed container is adiabatically and quasi-statically expanded from a state A (3 MPa, 2 L) to a state B with volume of 6 L along the path $1.8 pV = \text{constant}$. (a) Plot the path in the pV plane. (b) Find the amount of work done by the gas and the change in the internal energy of the gas during the process.

Solution:

a.



;

b. $W = 4.39 \text{ kJ}$, $\Delta E_{\text{int}} = -4.39 \text{ kJ}$

Glossary

first law of thermodynamics

the change in internal energy for any transition between two equilibrium states is $\Delta E_{\text{int}} = Q - W$

Thermodynamic Processes

By the end of this section, you will be able to:

- Define a thermodynamic process
- Distinguish between quasi-static and non-quasi-static processes
- Calculate physical quantities, such as the heat transferred, work done, and internal energy change for isothermal, adiabatic, and cyclical thermodynamic processes

In solving mechanics problems, we isolate the body under consideration, analyze the external forces acting on it, and then use Newton's laws to predict its behavior. In thermodynamics, we take a similar approach. We start by identifying the part of the universe we wish to study; it is also known as our system. (We defined a system at the beginning of this chapter as anything whose properties are of interest to us; it can be a single atom or the entire Earth.) Once our system is selected, we determine how the environment, or surroundings, interact with the system. Finally, with the interaction understood, we study the thermal behavior of the system with the help of the laws of thermodynamics.

The thermal behavior of a system is described in terms of *thermodynamic variables*. For an ideal gas, these variables are pressure, volume, temperature, and the number of molecules or moles of the gas. Different types of systems are generally characterized by different sets of variables. For example, the thermodynamic variables for a stretched rubber band are tension, length, temperature, and mass.

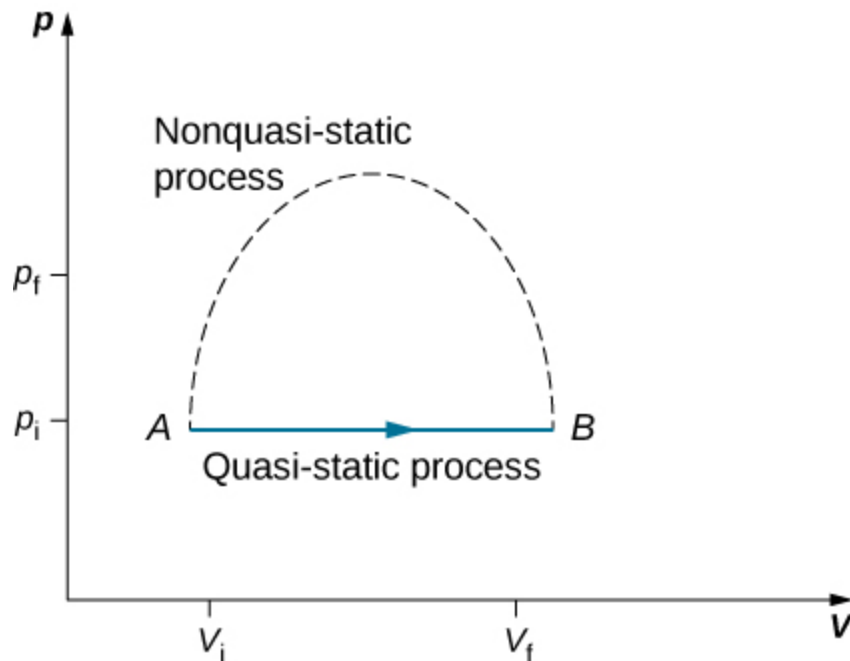
The state of a system can change as a result of its interaction with the environment. The change in a system can be fast or slow and large or small. The manner in which a state of a system can change from an initial state to a final state is called a **thermodynamic process**. For analytical purposes in thermodynamics, it is helpful to divide up processes as either *quasi-static* or *non-quasi-static*, as we now explain.

Quasi-static and Non-quasi-static Processes

A quasi-static process refers to an idealized or imagined process where the change in state is made infinitesimally slowly so that at each instant, the system can be assumed to be at a thermodynamic equilibrium with itself and with the environment. For instance, imagine heating 1 kg of water from a temperature 20°C to 21°C at a constant pressure of 1 atmosphere. To heat the water very slowly, we may imagine placing the container with water in a large bath that can be slowly heated such that the temperature of the bath can rise infinitesimally slowly from 20°C to 21°C . If we put 1 kg of water at 20°C directly into a bath at 21°C , the temperature of the water will rise rapidly to 21°C in a non-quasi-static way.

Quasi-static processes are done slowly enough that the system remains at thermodynamic equilibrium at each instant, despite the fact that the system changes over time. The thermodynamic equilibrium of the system is necessary for the system to have well-defined values of macroscopic properties such as the temperature and the pressure of the system at each instant of the process. Therefore, quasi-static processes can be shown as well-defined paths in state space of the system.

Since quasi-static processes cannot be completely realized for any finite change of the system, all processes in nature are non-quasi-static. Examples of quasi-static and non-quasi-static processes are shown in [\[link\]](#). Despite the fact that all finite changes must occur essentially non-quasi-statically at some stage of the change, we can imagine performing infinitely many quasi-static process corresponding to every quasi-static process. Since quasi-static processes can be analyzed analytically, we mostly study quasi-static processes in this book. We have already seen that in a quasi-static process the work by a gas is given by $p dV$.

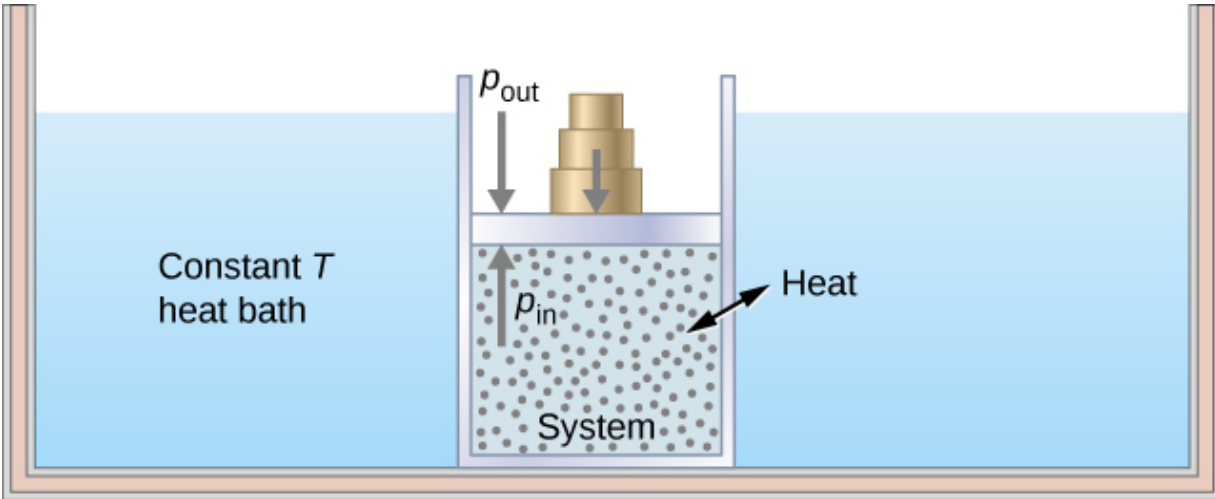


Quasi-static and non-quasi-static processes between states A and B of a gas. In a quasi-static process, the path of the process between A and B can be drawn in a state diagram since all the states that the system goes through are known. In a non-quasi-static process, the states between A and B are not known, and hence no path can be drawn. It may follow the dashed line as shown in the figure or take a very different path.

Isothermal Processes

An **isothermal process** is a change in the state of the system at a constant temperature. This process is accomplished by keeping the system in thermal equilibrium with a large heat bath during the process. Recall that a heat bath is an idealized “infinitely” large system whose temperature does not change. In practice, the temperature of a finite bath is controlled by either adding or removing a finite amount of energy as the case may be.

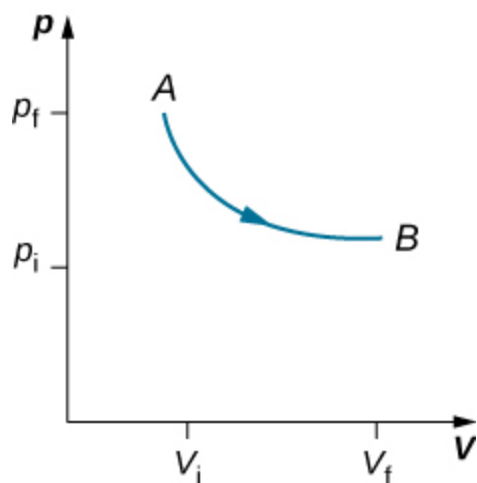
As an illustration of an isothermal process, consider a cylinder of gas with a movable piston immersed in a large water tank whose temperature is maintained constant. Since the piston is freely movable, the pressure inside p_{in} is balanced by the pressure outside p_{out} by some weights on the piston, as in [\[link\]](#).



Expanding a system at a constant temperature. Removing weights on the piston leads to an imbalance of forces on the piston, which causes the piston to move up. As the piston moves up, the temperature is lowered momentarily, which causes heat to flow from the heat bath to the system. The energy to move the piston eventually comes from the heat bath.

As weights on the piston are removed, an imbalance of forces on the piston develops. The net nonzero force on the piston would cause the piston to accelerate, resulting in an increase in volume. The expansion of the gas cools the gas to a lower temperature, which makes it possible for the heat to enter from the heat bath into the system until the temperature of the gas is reset to the temperature of the heat bath. If weights are removed in infinitesimal steps, the pressure in the system decreases infinitesimally slowly. This way, an isothermal process can be conducted quasi-statically. An isothermal line on a (p, V) diagram is represented by a curved line from

starting point A to finishing point B , as seen in [\[link\]](#). For an ideal gas, an isothermal process is hyperbolic, since for an ideal gas at constant temperature, $p \propto \frac{1}{V}$.



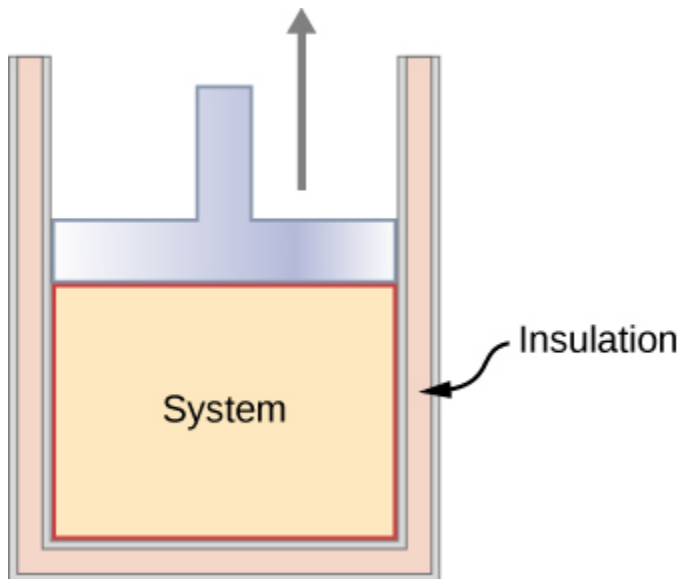
An isothermal expansion from a state labeled A to another state labeled B on a pV diagram. The curve represents the relation between pressure and volume in an ideal gas at constant temperature.

An isothermal process studied in this chapter is quasi-statically performed, since to be isothermal throughout the change of volume, you must be able to state the temperature of the system at each step, which is possible only if the system is in thermal equilibrium continuously. The system must go out of equilibrium for the state to change, but for quasi-static processes, we imagine that the process is conducted in infinitesimal steps such that these departures from equilibrium can be made as brief and as small as we like.

Other quasi-static processes of interest for gases are isobaric and isochoric processes. An **isobaric process** is a process where the pressure of the system does not change, whereas an **isochoric process** is a process where the volume of the system does not change.

Adiabatic Processes

In an **adiabatic process**, the system is insulated from its environment so that although the state of the system changes, no heat is allowed to enter or leave the system, as seen in [\[link\]](#). An adiabatic process can be conducted either quasi-statically or non-quasi-statically. When a system expands adiabatically, it must do work against the outside world, and therefore its energy goes down, which is reflected in the lowering of the temperature of the system. An adiabatic expansion leads to a lowering of temperature, and an adiabatic compression leads to an increase of temperature. We discuss adiabatic expansion again in [Adiabatic Processes for an ideal Gas](#).



An insulated piston with a hot, compressed gas is released. The piston moves up, the volume expands, and the pressure and temperature decrease. The internal

energy goes into work. If the expansion occurs within a time frame in which negligible heat can enter the system, then the process is called adiabatic. Ideally, during an adiabatic process no heat enters or exits the system.

Cyclic Processes

We say that a system goes through a **cyclic process** if the state of the system at the end is same as the state at the beginning. Therefore, state properties such as temperature, pressure, volume, and internal energy of the system do not change over a complete cycle:

Equation:

$$\Delta_{\text{int}} = 0.$$

When the first law of thermodynamics is applied to a cyclic process, we obtain a simple relation between heat into the system and the work done by the system over the cycle:

Equation:

$$= \quad (\text{cyclic process}).$$

Thermodynamic processes are also distinguished by whether or not they are reversible. A **reversible process** is one that can be made to retrace its path by differential changes in the environment. Such a process must therefore also be quasi-static. Note, however, that a quasi-static process is not necessarily reversible, since there may be dissipative forces involved. For example, if friction occurred between the piston and the walls of the cylinder containing the gas, the energy lost to friction would prevent us from reproducing the original states of the system.

We considered several thermodynamic processes:

1. An isothermal process, during which the system's temperature remains constant
2. An adiabatic process, during which no heat is transferred to or from the system
3. An isobaric process, during which the system's pressure does not change
4. An isochoric process, during which the system's volume does not change

Many other processes also occur that do not fit into any of these four categories.

Note:

View this [site](#) to set up your own process in a pV diagram. See if you can calculate the values predicted by the simulation for heat, work, and change in internal energy.

Summary

- The thermal behavior of a system is described in terms of thermodynamic variables. For an ideal gas, these variables are pressure, volume, temperature, and number of molecules or moles of the gas.
- For systems in thermodynamic equilibrium, the thermodynamic variables are related by an equation of state.
- A heat reservoir is so large that when it exchanges heat with other systems, its temperature does not change.
- A quasi-static process takes place so slowly that the system involved is always in thermodynamic equilibrium.
- A reversible process is one that can be made to retrace its path and both the temperature and pressure are uniform throughout the system.

- There are several types of thermodynamic processes, including (a) isothermal, where the system's temperature is constant; (b) adiabatic, where no heat is exchanged by the system; (c) isobaric, where the system's pressure is constant; and (d) isochoric, where the system's volume is constant.
- As a consequence of the first law of thermodynamics, here is a summary of the thermodynamic processes: (a) isothermal: $\Delta_{\text{int}} = 0$, $Q = W$; (b) adiabatic: $Q = 0$, $\Delta_{\text{int}} = -W$; (c) isobaric: $\Delta_{\text{int}} = nC_p \Delta T$; and (d) isochoric: $W = 0$, $\Delta_{\text{int}} = Q$.

Conceptual Questions

Exercise:

Problem:

When a gas expands isothermally, it does work. What is the source of energy needed to do this work?

Solution:

The system must be in contact with a heat source that allows heat to flow into the system.

Exercise:

Problem:

If the pressure and volume of a system are given, is the temperature always uniquely determined?

Exercise:

Problem:

It is unlikely that a process can be isothermal unless it is a very slow process. Explain why. Is the same true for isobaric and isochoric processes? Explain your answer.

Solution:

Isothermal processes must be slow to make sure that as heat is transferred, the temperature does not change. Even for isobaric and isochoric processes, the system must be in thermal equilibrium with slow changes of thermodynamic variables.

Problems

Exercise:

Problem:

Two moles of a monatomic ideal gas at (5 MPa, 5 L) is expanded isothermally until the volume is doubled (step 1). Then it is cooled isochorically until the pressure is 1 MPa (step 2). The temperature drops in this process. The gas is now compressed isothermally until its volume is back to 5 L, but its pressure is now 2 MPa (step 3). Finally, the gas is heated isochorically to return to the initial state (step 4). (a) Draw the four processes in the pV plane. (b) Find the total work done by the gas.

Exercise:

Problem:

Consider a transformation from point A to B in a two-step process. First, the pressure is lowered from 3 MPa at point A to a pressure of 1 MPa, while keeping the volume at 2 L by cooling the system. The state reached is labeled C . Then the system is heated at a constant pressure to reach a volume of 6 L in the state B . (a) Find the amount of work done on the ACB path. (b) Find the amount of heat exchanged by the system when it goes from A to B on the ACB path. (c) Compare the change in the internal energy when the AB process occurs adiabatically with the AB change through the two-step process on the ACB path.

Solution:

a. 1660 J; b. -2730 J; c. It does not depend on the process.

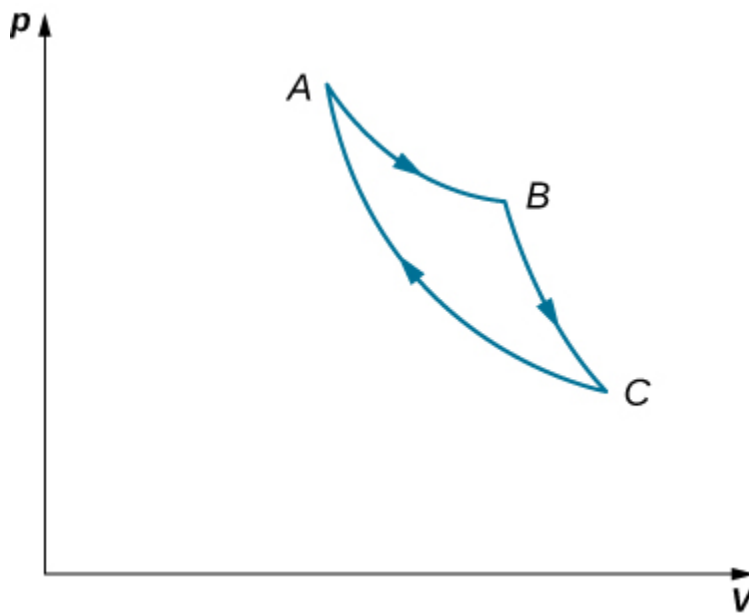
Exercise:

Problem:

Consider a cylinder with a movable piston containing n moles of an ideal gas. The entire apparatus is immersed in a constant temperature bath of temperature T kelvin. The piston is then pushed slowly so that the pressure of the gas changes quasi-statically from p_1 to p_2 at constant temperature T . Find the work done by the gas in terms of n , R , T , p_1 , and p_2 .

Exercise:**Problem:**

An ideal gas expands isothermally along AB and does 700 J of work (see below). (a) How much heat does the gas exchange along AB? (b) The gas then expands adiabatically along BC and does 400 J of work. When the gas returns to A along CA, it exhausts 100 J of heat to its surroundings. How much work is done on the gas along this path?



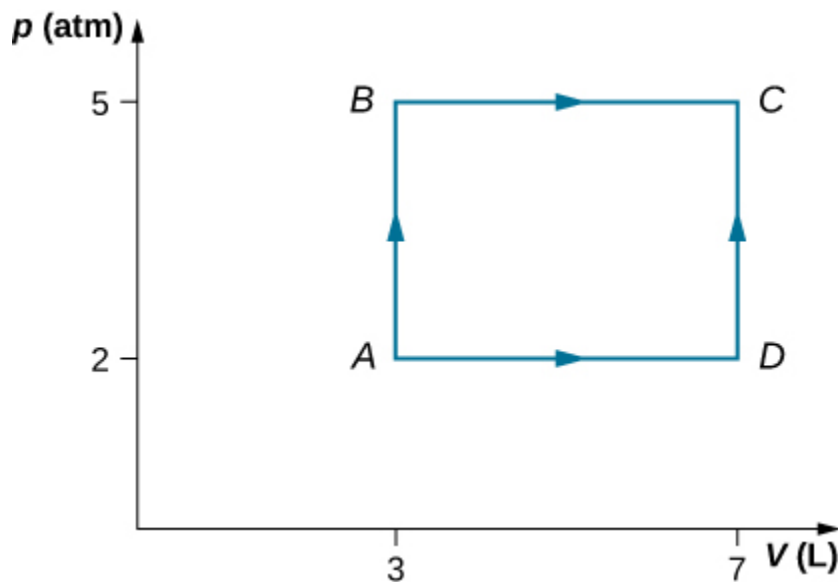
Solution:

a. 700 J; b. 500 J

Exercise:

Problem:

Consider the processes shown below. In the processes AB and BC, 3600 J and 2400 J of heat are added to the system, respectively. (a) Find the work done in each of the processes AB, BC, AD, and DC. (b) Find the internal energy change in processes AB and BC. (c) Find the internal energy difference between states C and A. (d) Find the total heat added in the ADC process. (e) From the information give, can you find the heat added in process AD? Why or why not?

**Exercise:****Problem:**

Two moles of helium gas are placed in a cylindrical container with a piston. The gas is at room temperature 25°C and under a pressure of $3.0 \times 10^5 \text{ Pa}$. When the pressure from the outside is decreased while keeping the temperature the same as the room temperature, the volume of the gas doubles. (a) Find the work the external agent does on the gas in the process. (b) Find the heat exchanged by the gas and indicate whether the gas takes in or gives up heat. Assume ideal gas behavior.

Solution:

a. -3400 J ; b. 3400 J enters the gas

Exercise:

Problem:

An amount of n moles of a monatomic ideal gas in a conducting container with a movable piston is placed in a large thermal heat bath at temperature T_1 and the gas is allowed to come to equilibrium. After the equilibrium is reached, the pressure on the piston is lowered so that the gas expands at constant temperature. The process is continued quasi-statically until the final pressure is $4/3$ of the initial pressure P_1 . (a) Find the change in the internal energy of the gas. (b) Find the work done by the gas. (c) Find the heat exchanged by the gas, and indicate, whether the gas takes in or gives up heat.

Glossary

adiabatic process

process during which no heat is transferred to or from the system

cyclic process

process in which the state of the system at the end is same as the state at the beginning

isobaric process

process during which the system's pressure does not change

isochoric process

process during which the system's volume does not change

isothermal process

process during which the system's temperature remains constant

reversible process

process that can be reverted to restore both the system and its environment back to their original states together

thermodynamic process

manner in which a state of a system can change from initial state to final state

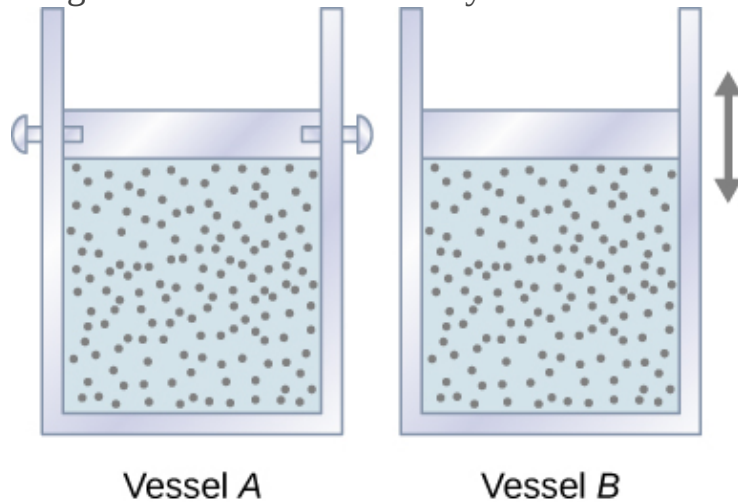
Heat Capacities of an Ideal Gas

By the end of this section, you will be able to:

- Define heat capacity of an ideal gas for a specific process
- Calculate the specific heat of an ideal gas for either an isobaric or isochoric process
- Explain the difference between the heat capacities of an ideal gas and a real gas
- Estimate the change in specific heat of a gas over temperature ranges

We learned about specific heat and molar heat capacity in [Temperature and Heat](#); however, we have not considered a process in which heat is added. We do that in this section. First, we examine a process where the system has a constant volume, then contrast it with a system at constant pressure and show how their specific heats are related.

Let's start with looking at [\[link\]](#), which shows two vessels *A* and *B*, each containing 1 mol of the same type of ideal gas at a temperature T and a volume V . The only difference between the two vessels is that the piston at the top of *A* is fixed, whereas the one at the top of *B* is free to move against a constant external pressure p . We now consider what happens when the temperature of the gas in each vessel is slowly increased to $T + dT$ with the addition of heat.



Two vessels are identical except that the piston at the top of *A* is fixed, whereas that at *B* is free to move against a constant external pressure p .

Since the piston of vessel *A* is fixed, the volume of the enclosed gas does not change. Consequently, the gas does no work, and we have from the first law

Equation:

$$dE_{\text{int}} = dQ - dW = dQ.$$

We represent the fact that the heat is exchanged at constant volume by writing

Equation:

$$dQ = C_V dT,$$

where C_V is the **molar heat capacity at constant volume** of the gas. In addition, since $dE_{\text{int}} = dQ$ for this particular process,

Equation:

$$dE_{\text{int}} = C_V dT.$$

We obtained this equation assuming the volume of the gas was fixed. However, internal energy is a state function that depends on only the temperature of an ideal gas. Therefore, $dE_{\text{int}} = C_V dT$ gives the change in internal energy of an ideal gas for any process involving a temperature change dT .

When the gas in vessel *B* is heated, it expands against the movable piston and does work $dW = p dV$. In this case, the heat is added at constant pressure, and we write

Equation:

$$dQ = C_p dT,$$

where C_p is the **molar heat capacity at constant pressure** of the gas. Furthermore, since the ideal gas expands against a constant pressure,

Equation:

$$d(pV) = d(RT)$$

becomes

Equation:

$$pdV = RdT.$$

Finally, inserting the expressions for dQ and pdV into the first law, we obtain

Equation:

$$dE_{\text{int}} = dQ - pdV = (C_p - R)dT.$$

We have found dE_{int} for both an isochoric and an isobaric process. Because the internal energy of an ideal gas depends only on the temperature, dE_{int} must be the same for both processes. Thus,

Equation:

$$C_V dT = (C_p - R)dT,$$

and

Note:

Equation:

$$C_p = C_V + R.$$

The derivation of [\[link\]](#) was based only on the ideal gas law. Consequently, this relationship is approximately valid for all dilute gases, whether monatomic like He, diatomic like O₂, or polyatomic like CO₂ or NH₃.

In the preceding chapter, we found the molar heat capacity of an ideal gas under constant volume to be

Equation:

$$C_V = \frac{d}{2}R,$$

where d is the number of degrees of freedom of a molecule in the system. [\[link\]](#) shows the molar heat capacities of some dilute ideal gases at room temperature. The heat capacities of real gases are somewhat higher than those predicted by the expressions of C_V and C_p given in [\[link\]](#). This indicates that vibrational motion in polyatomic molecules is significant, even at room temperature. Nevertheless, the difference in the molar heat capacities, $C_p - C_V$, is very close to R , even for the polyatomic gases.

Molar Heat Capacities of Dilute Ideal Gases at Room Temperature				
Type of Molecule	Gas	C_p (J/mol K)	C_V (J/mol K)	$C_p - C_V$ (J/mol K)
Monatomic	Ideal	$\frac{5}{2}R = 20.79$	$\frac{3}{2}R = 12.47$	$R = 8.31$
Diatomic	Ideal	$\frac{7}{2}R = 29.10$	$\frac{5}{2}R = 20.79$	$R = 8.31$
Polyatomic	Ideal	$4R = 33.26$	$3R = 24.94$	$R = 8.31$

Summary

- For an ideal gas, the molar capacity at constant pressure C_p is given by $C_p = C_V + R = dR/2 + R$, where d is the number of degrees of freedom of each molecule/entity in the system.
- A real gas has a specific heat close to but a little bit higher than that of the corresponding ideal gas with $C_p \simeq C_V + R$.

Conceptual Questions

Exercise:

Problem:

How can an object transfer heat if the object does not possess a discrete quantity of heat?

Exercise:

Problem:

Most materials expand when heated. One notable exception is water between $0\text{ }^{\circ}\text{C}$ and $4\text{ }^{\circ}\text{C}$, which actually decreases in volume with the increase in temperature. Which is greater for water in this temperature region, C_p or C_V ?

Solution:

Typically C_p is greater than C_V because when expansion occurs under constant pressure, it does work on the surroundings. Therefore, heat can go into internal energy and work. Under constant volume, all heat goes into internal energy. In this example, water contracts upon heating, so if we add heat at constant pressure, work is done on the water by surroundings and therefore, C_p is less than C_V .

Exercise:

Problem:

Why are there two specific heats for gases C_p and C_V , yet only one given for solid?

Problems

Exercise:

Problem:

The temperature of an ideal monatomic gas rises by 8.0 K . What is the change in the internal energy of 1 mol of the gas at constant volume?

Solution:

100 J

Exercise:**Problem:**

For a temperature increase of $10\text{ }^{\circ}\text{C}$ at constant volume, what is the heat absorbed by (a) 3.0 mol of a dilute monatomic gas; (b) 0.50 mol of a dilute diatomic gas; and (c) 15 mol of a dilute polyatomic gas?

Exercise:**Problem:**

If the gases of the preceding problem are initially at 300 K, what are their internal energies after they absorb the heat?

Solution:

a. 370 J; b. 100 J; c. 500 J

Exercise:**Problem:**

Consider 0.40 mol of dilute carbon dioxide at a pressure of 0.50 atm and a volume of 50 L. What is the internal energy of the gas?

Exercise:**Problem:**

When 400 J of heat are slowly added to 10 mol of an ideal monatomic gas, its temperature rises by $10\text{ }^{\circ}\text{C}$. What is the work done on the gas?

Solution:

850 J

Exercise:

Problem:

One mole of a dilute diatomic gas occupying a volume of 10.00 L expands against a constant pressure of 2.000 atm when it is slowly heated. If the temperature of the gas rises by 10.00 K and 400.0 J of heat are added in the process, what is its final volume?

Glossary

molar heat capacity at constant pressure

quantifies the ratio of the amount of heat added removed to the temperature while measuring at constant pressure

molar heat capacity at constant volume

quantifies the ratio of the amount of heat added removed to the temperature while measuring at constant volume

Adiabatic Processes for an Ideal Gas

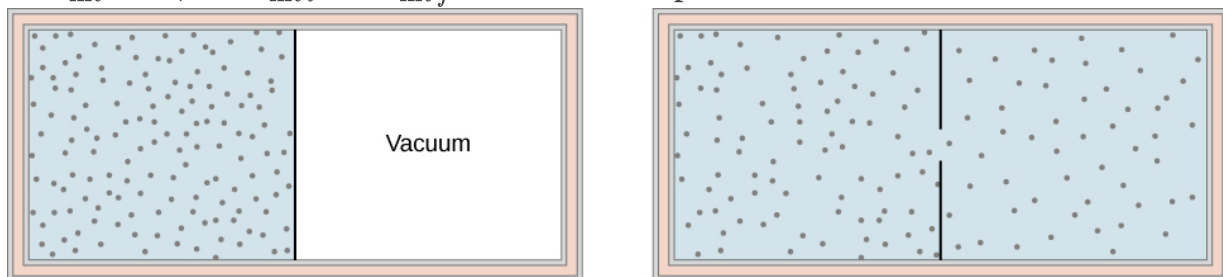
By the end of this section, you will be able to:

- Define adiabatic expansion of an ideal gas
- Demonstrate the qualitative difference between adiabatic and isothermal expansions

When an ideal gas is compressed adiabatically ($Q = 0$), work is done on it and its temperature increases; in an adiabatic expansion, the gas does work and its temperature drops. Adiabatic compressions actually occur in the cylinders of a car, where the compressions of the gas-air mixture take place so quickly that there is no time for the mixture to exchange heat with its environment.

Nevertheless, because work is done on the mixture during the compression, its temperature does rise significantly. In fact, the temperature increases can be so large that the mixture can explode without the addition of a spark. Such explosions, since they are not timed, make a car run poorly—it usually “knocks.” Because ignition temperature rises with the octane of gasoline, one way to overcome this problem is to use a higher-octane gasoline.

Another interesting adiabatic process is the free expansion of a gas. [\[link\]](#) shows a gas confined by a membrane to one side of a two-compartment, thermally insulated container. When the membrane is punctured, gas rushes into the empty side of the container, thereby expanding freely. Because the gas expands “against a vacuum” ($p = 0$), it does no work, and because the vessel is thermally insulated, the expansion is adiabatic. With $Q = 0$ and $W = 0$ in the first law, $\Delta E_{\text{int}} = 0$, so $E_{\text{int}i} = E_{\text{int}f}$ for the free expansion.



Initial equilibrium state

Final equilibrium state

The gas in the left chamber expands freely into the right chamber when the membrane is punctured.

If the gas is ideal, the internal energy depends only on the temperature. Therefore, when an ideal gas expands freely, its temperature does not change.

A quasi-static, adiabatic expansion of an ideal gas is represented in [\[link\]](#), which shows an insulated cylinder that contains 1 mol of an ideal gas. The gas is made to expand quasi-statically by removing one grain of sand at a time from the top of the piston. When the gas expands by dV , the change in its temperature is dT . The work done by the gas in the expansion is $dW = pdV$; $dQ = 0$ because the cylinder is insulated; and the change in the internal energy of the gas is, from [\[link\]](#), $dE_{\text{int}} = C_V dT$. Therefore, from the first law,

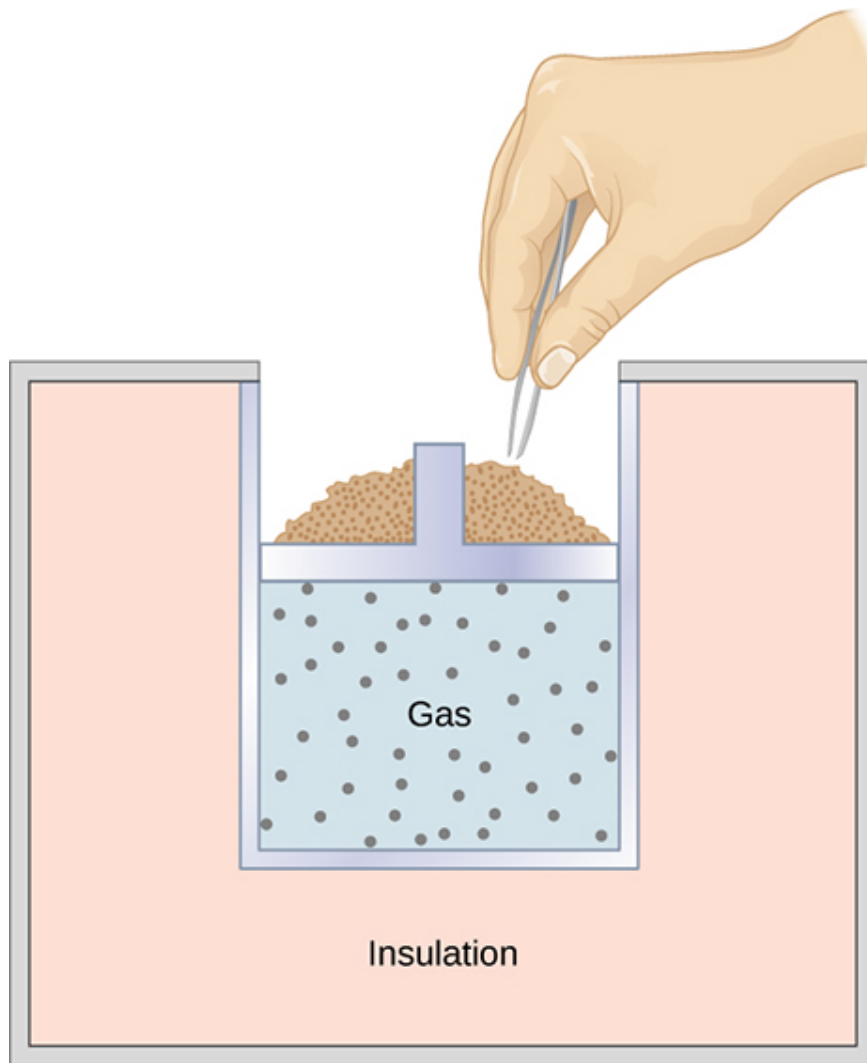
Equation:

$$C_V dT = 0 - pdV = -pdV,$$

so

Equation:

$$dT = -\frac{pdV}{C_V}.$$



When sand is removed from the piston one grain at a time, the gas expands adiabatically and quasi-statically in the insulated vessel.

Also, for 1 mol of an ideal gas,

Equation:

$$d(pV) = d(RT),$$

so

Equation:

$$pdV + Vdp = RdT$$

and

Equation:

$$dT = \frac{pdV + Vdp}{R}.$$

We now have two equations for dT . Upon equating them, we find that

Equation:

$$C_V V dp + (C_V + R) p dV = 0.$$

Now, we divide this equation by pV and use $C_p = C_V + R$. We are then left with

Equation:

$$C_V \frac{dp}{p} + C_p \frac{dV}{V} = 0,$$

which becomes

Equation:

$$\frac{dp}{p} + \gamma \frac{dV}{V} = 0,$$

where we define γ as the ratio of the molar heat capacities:

Note:

Equation:

$$\gamma = \frac{C_p}{C_V}.$$

Thus,

Equation:

$$\int \frac{dp}{p} + \gamma \int \frac{dV}{V} = 0$$

and

Equation:

$$\ln p + \gamma \ln V = \text{constant}.$$

Finally, using $\ln(A^x) = x \ln A$ and $\ln AB = \ln A + \ln B$, we can write this in the form

Note:

Equation:

$$pV^\gamma = \text{constant}.$$

This equation is the condition that must be obeyed by an ideal gas in a quasi-static adiabatic process. For example, if an ideal gas makes a quasi-static adiabatic transition from a state with pressure and volume p_1 and V_1 to a state with p_2 and V_2 , then it must be true that $p_1 V_1^\gamma = p_2 V_2^\gamma$.

The adiabatic condition of [\[link\]](#) can be written in terms of other pairs of thermodynamic variables by combining it with the ideal gas law. In doing this, we find that

Equation:

$$p^{1-\gamma} T^\gamma = \text{constant}$$

and

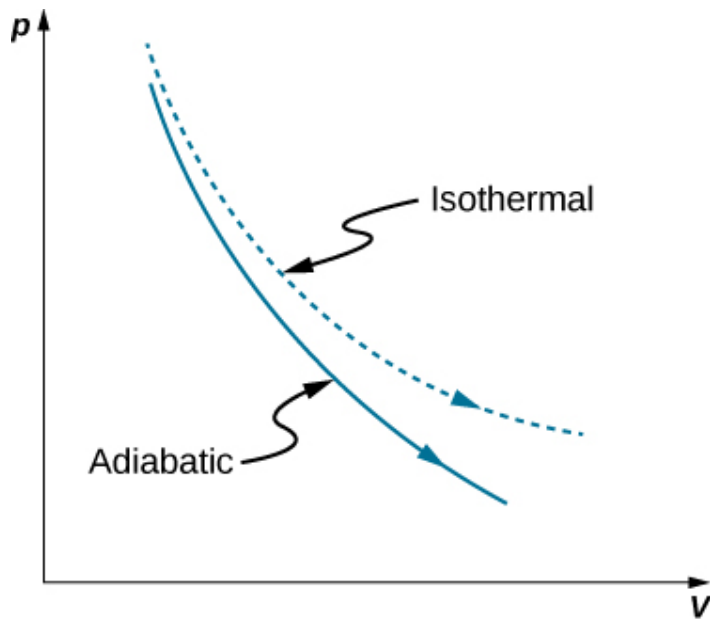
Equation:

$$TV^{\gamma-1} = \text{constant}.$$

A reversible adiabatic expansion of an ideal gas is represented on the pV diagram of [\[link\]](#). The slope of the curve at any point is

Equation:

$$\frac{dp}{dV} = \frac{d}{dV} \left(\frac{\text{constant}}{V^{\gamma}} \right) = -\gamma \frac{p}{V}.$$



Quasi-static adiabatic and isothermal expansions of an ideal gas.

The dashed curve shown on this pV diagram represents an isothermal expansion where T (and therefore pV) is constant. The slope of this curve is useful when we consider the second law of thermodynamics in the next chapter. This slope is

Equation:

$$\frac{dp}{dV} = \frac{d}{dV} \frac{nRT}{V} = -\frac{p}{V}.$$

Because $\gamma > 1$, the isothermal curve is not as steep as that for the adiabatic expansion.

Example:

Compression of an Ideal Gas in an Automobile Engine

Gasoline vapor is injected into the cylinder of an automobile engine when the piston is in its expanded position. The temperature, pressure, and volume of the resulting gas-air mixture are 20°C , $1.00 \times 10^5 \text{ N/m}^2$, and 240 cm^3 , respectively. The mixture is then compressed adiabatically to a volume of 40 cm^3 . Note that in the actual operation of an automobile engine, the compression is not quasi-static, although we are making that assumption here.

(a) What are the pressure and temperature of the mixture after the compression?

(b) How much work is done by the mixture during the compression?

Strategy

Because we are modeling the process as a quasi-static adiabatic compression of an ideal gas, we have $pV^\gamma = \text{constant}$ and $pV = nRT$. The work needed can

then be evaluated with $W = \int_{V_1}^{V_2} p dV$.

Solution

a. For an adiabatic compression we have

Equation:

$$p_2 = p_1 \left(\frac{V_1}{V_2} \right)^\gamma,$$

so after the compression, the pressure of the mixture is

Equation:

$$p_2 = (1.00 \times 10^5 \text{ N/m}^2) \left(\frac{240 \times 10^{-6} \text{ m}^3}{40 \times 10^{-6} \text{ m}^3} \right)^{1.40} = 1.23 \times 10^6 \text{ N/m}^2.$$

From the ideal gas law, the temperature of the mixture after the compression is

Equation:

$$\begin{aligned}
 T_2 &= \left(\frac{p_2 V_2}{p_1 V_1} \right) T_1 \\
 &= \frac{(1.23 \times 10^6 \text{ N/m}^2)(40 \times 10^{-6} \text{ m}^3)}{(1.00 \times 10^5 \text{ N/m}^2)(240 \times 10^{-6} \text{ m}^3)} \cdot 293 \text{ K} \\
 &= 600 \text{ K} = 328^\circ \text{C}.
 \end{aligned}$$

b. The work done by the mixture during the compression is

Equation:

$$W = \int_{V_1}^{V_2} p dV.$$

With the adiabatic condition of [\[link\]](#), we may write p as K/V^γ , where $K = p_1 V_1^\gamma = p_2 V_2^\gamma$. The work is therefore

Equation:

$$\begin{aligned}
 W &= \int_{V_1}^{V_2} \frac{K}{V^\gamma} dV \\
 &= \frac{K}{1-\gamma} \left(\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right) \\
 &= \frac{1}{1-\gamma} \left(\frac{p_2 V_2^\gamma}{V_2^{\gamma-1}} - \frac{p_1 V_1^\gamma}{V_1^{\gamma-1}} \right) \\
 &= \frac{1}{1-\gamma} (p_2 V_2 - p_1 V_1) \\
 &= \frac{1}{1-1.40} [(1.23 \times 10^6 \text{ N/m}^2)(40 \times 10^{-6} \text{ m}^3) \\
 &\quad - (1.00 \times 10^5 \text{ N/m}^2)(240 \times 10^{-6} \text{ m}^3)] \\
 &= -63 \text{ J}.
 \end{aligned}$$

Significance

The negative sign on the work done indicates that the piston does work on the gas-air mixture. The engine would not work if the gas-air mixture did work on the piston.

Summary

- A quasi-static adiabatic expansion of an ideal gas produces a steeper pV curve than that of the corresponding isotherm.
- A realistic expansion can be adiabatic but rarely quasi-static.

Key Equations

Equation of state for a closed system	$f(p, V, T) = 0$
Net work for a finite change in volume	$W = \int_{V_1}^{V_2} p dV$
Internal energy of a system (average total energy)	$E_{\text{int}} = \sum_i (K_i + U_i),$
Internal energy of a monatomic ideal gas	$E_{\text{int}} = nN_A \left(\frac{3}{2} k_B T \right) = \frac{3}{2} nRT$
First law of thermodynamics	$\Delta E_{\text{int}} = Q - W$
Molar heat capacity at constant pressure	$C_p = C_V + R$
Ratio of molar heat capacities	$\gamma = C_p / C_V$
Condition for an ideal gas in a quasi-static adiabatic process	$pV^\gamma = \text{constant}$

Conceptual Questions

Exercise:

Problem: Is it possible for γ to be smaller than unity?

Solution:

No, it is always greater than 1.

Exercise:

Problem: Would you expect γ to be larger for a gas or a solid? Explain.

Exercise:**Problem:**

There is no change in the internal energy of an ideal gas undergoing an isothermal process since the internal energy depends only on the temperature. Is it therefore correct to say that an isothermal process is the same as an adiabatic process for an ideal gas? Explain your answer.

Solution:

An adiabatic process has a change in temperature but no heat flow. The isothermal process has no change in temperature but has heat flow.

Exercise:**Problem:**

Does a gas do any work when it expands adiabatically? If so, what is the source of the energy needed to do this work?

Problems**Exercise:****Problem:**

A monatomic ideal gas undergoes a quasi-static adiabatic expansion in which its volume is doubled. How is the pressure of the gas changed?

Solution:

pressure decreased by 0.31 times the original pressure

Exercise:**Problem:**

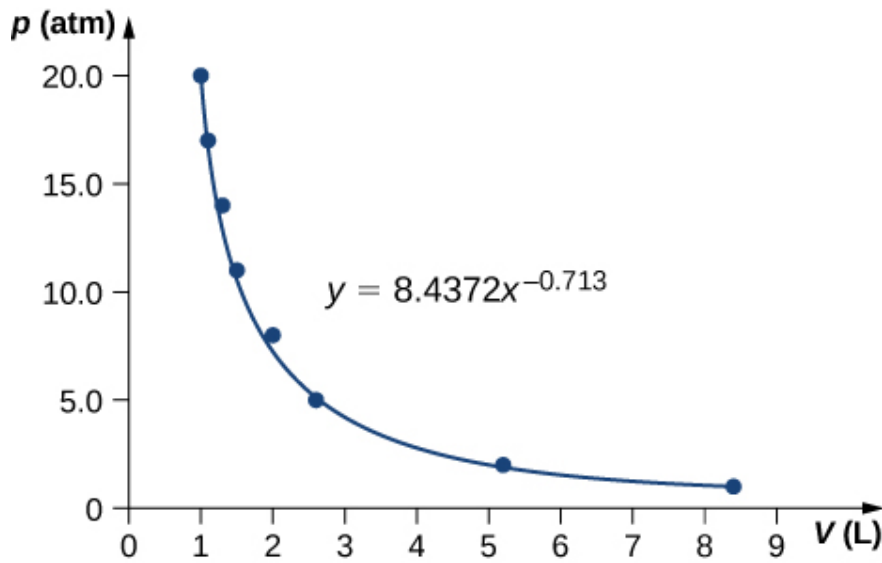
An ideal gas has a pressure of 0.50 atm and a volume of 10 L. It is compressed adiabatically and quasi-statically until its pressure is 3.0 atm and its volume is 2.8 L. Is the gas monatomic, diatomic, or polyatomic?

Exercise:**Problem:**

Pressure and volume measurements of a dilute gas undergoing a quasi-static adiabatic expansion are shown below. Plot $\ln p$ vs. V and determine γ for this gas from your graph.

P (atm)	V (L)
20.0	1.0
17.0	1.1
14.0	1.3
11.0	1.5
8.0	2.0
5.0	2.6
2.0	5.2
1.0	8.4

Solution:



;

$$\gamma = 0.713$$

Exercise:

Problem:

An ideal monatomic gas at 300 K expands adiabatically and reversibly to twice its volume. What is its final temperature?

Exercise:

Problem:

An ideal diatomic gas at 80 K is slowly compressed adiabatically and reversibly to twice its volume. What is its final temperature?

Solution:

84 K

Exercise:

Problem:

An ideal diatomic gas at 80 K is slowly compressed adiabatically to one-third its original volume. What is its final temperature?

Exercise:**Problem:**

Compare the change in internal energy of an ideal gas for a quasi-static adiabatic expansion with that for a quasi-static isothermal expansion. What happens to the temperature of an ideal gas in an adiabatic expansion?

Solution:

An adiabatic expansion has less work done and no heat flow, thereby a lower internal energy comparing to an isothermal expansion which has both heat flow and work done. Temperature decreases during adiabatic expansion.

Exercise:**Problem:**

The temperature of n moles of an ideal gas changes from T_1 to T_2 in a quasi-static adiabatic transition. Show that the work done by the gas is given by

$$W = \frac{nR}{\gamma-1}(T_1 - T_2).$$

Exercise:**Problem:**

A dilute gas expands quasi-statically to three times its initial volume. Is the final gas pressure greater for an isothermal or an adiabatic expansion? Does your answer depend on whether the gas is monatomic, diatomic, or polyatomic?

Solution:

Isothermal has a greater final pressure and does not depend on the type of gas.

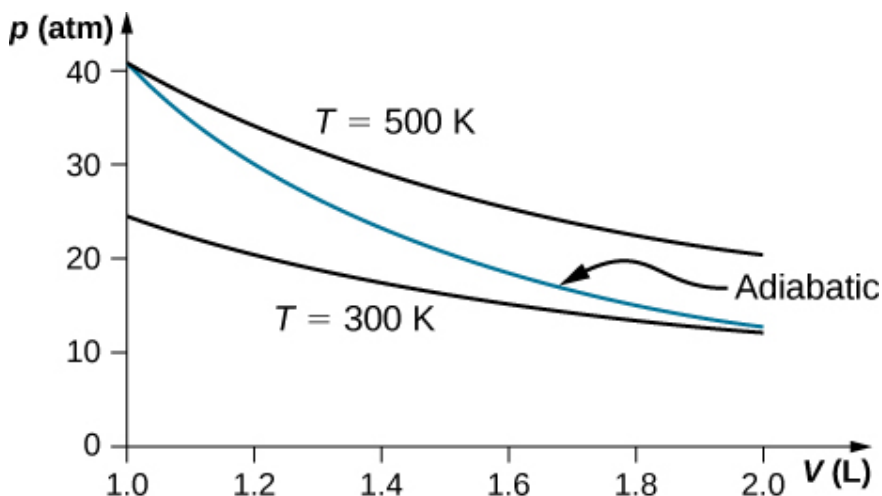
Exercise:

Problem:

(a) An ideal gas expands adiabatically from a volume of $2.0 \times 10^{-3} \text{ m}^3$ to $2.5 \times 10^{-3} \text{ m}^3$. If the initial pressure and temperature were $5.0 \times 10^5 \text{ Pa}$ and 300 K , respectively, what are the final pressure and temperature of the gas? Use $\gamma = 5/3$ for the gas. (b) In an isothermal process, an ideal gas expands from a volume of $2.0 \times 10^{-3} \text{ m}^3$ to $2.5 \times 10^{-3} \text{ m}^3$. If the initial pressure and temperature were $5.0 \times 10^5 \text{ Pa}$ and 300 K , respectively, what are the final pressure and temperature of the gas?

Exercise:**Problem:**

On an adiabatic process of an ideal gas pressure, volume and temperature change such that pV^γ is constant with $\gamma = 5/3$ for monatomic gas such as helium and $\gamma = 7/5$ for diatomic gas such as hydrogen at room temperature. Use numerical values to plot two isotherms of 1 mol of helium gas using ideal gas law and two adiabatic processes mediating between them. Use $T_1 = 500 \text{ K}$, $V_1 = 1 \text{ L}$, and $T_2 = 300 \text{ K}$ for your plot.

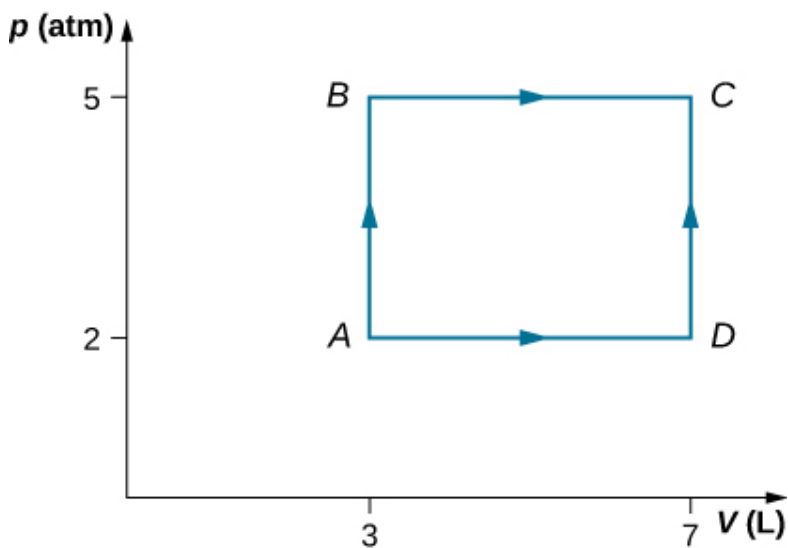
Solution:**Exercise:**

Problem:

Two moles of a monatomic ideal gas such as helium is compressed adiabatically and reversibly from a state (3 atm, 5 L) to a state with pressure 4 atm. (a) Find the volume and temperature of the final state. (b) Find the temperature of the initial state of the gas. (c) Find the work done by the gas in the process. (d) Find the change in internal energy of the gas in the process.

Additional Problems**Exercise:****Problem:**

Consider the process shown below. During steps AB and BC , 3600 J and 2400 J of heat, respectively, are added to the system. (a) Find the work done in each of the processes AB , BC , AD , and DC . (b) Find the internal energy change in processes AB and BC . (c) Find the internal energy difference between states C and A . (d) Find the total heat added in the ADC process. (e) From the information given, can you find the heat added in process AD ? Why or why not?



Solution:

a. $W_{AB} = 0$, $W_{BC} = 2026 \text{ J}$, $W_{AD} = 810.4 \text{ J}$, $W_{DC} = 0$; b. $\Delta E_{AB} = 3600 \text{ J}$, $\Delta E_{BC} = 374 \text{ J}$; c. $\Delta E_{AC} = 3974 \text{ J}$; d. $Q_{ADC} = 4784 \text{ J}$; e. No, because heat was added for both parts AD and DC . There is not enough information to figure out how much is from each segment of the path.

Exercise:

Problem:

A car tire contains 0.0380 m^3 of air at a pressure of $2.20 \times 10^5 \text{ Pa}$ (about 32 psi). How much more internal energy does this gas have than the same volume has at zero gauge pressure (which is equivalent to normal atmospheric pressure)?

Exercise:

Problem:

A helium-filled toy balloon has a gauge pressure of 0.200 atm and a volume of 10.0 L. How much greater is the internal energy of the helium in the balloon than it would be at zero gauge pressure?

Solution:

300 J

Exercise:

Problem:

Steam to drive an old-fashioned steam locomotive is supplied at a constant gauge pressure of $1.75 \times 10^6 \text{ N/m}^2$ (about 250 psi) to a piston with a 0.200-m radius. (a) By calculating $p\Delta V$, find the work done by the steam when the piston moves 0.800 m. Note that this is the net work output, since gauge pressure is used. (b) Now find the amount of work by calculating the force exerted times the distance traveled. Is the answer the same as in part (a)?

Exercise:

Problem:

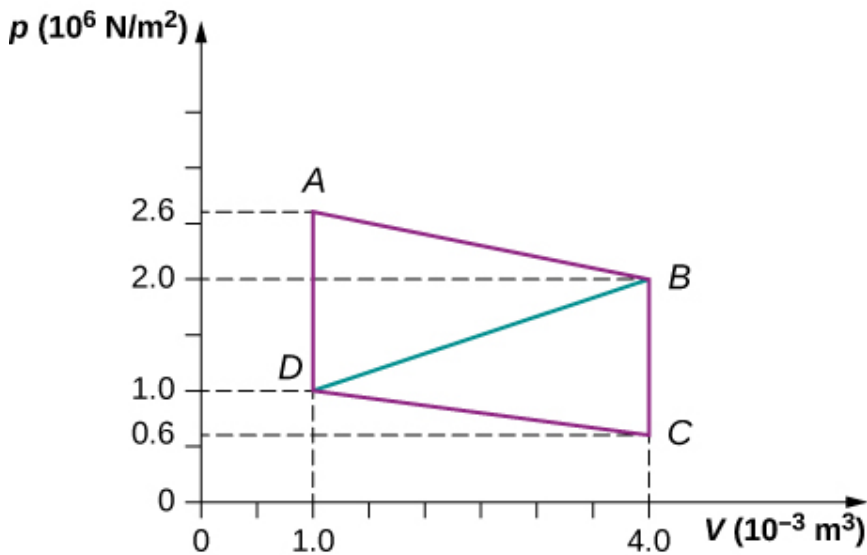
A hand-driven tire pump has a piston with a 2.50-cm diameter and a maximum stroke of 30.0 cm. (a) How much work do you do in one stroke if the average gauge pressure is $2.4 \times 10^5 \text{ N/m}^2$ (about 35 psi)? (b) What average force do you exert on the piston, neglecting friction and gravitational force?

Solution:

a. 59.5 J; b. 170 N

Exercise:**Problem:**

Calculate the net work output of a heat engine following path *ABCD*A as shown below.

**Exercise:****Problem:**

What is the net work output of a heat engine that follows path *ABDA* in the preceding problem with a straight line from *B* to *D*? Why is the work output less than for path *ABCD*A?

Solution:

$$2.4 \times 10^3 \text{ J}$$

Exercise:**Problem:**

Five moles of a monatomic ideal gas in a cylinder at 27°C is expanded isothermally from a volume of 5 L to 10 L. (a) What is the change in internal energy? (b) How much work was done on the gas in the process? (c) How much heat was transferred to the gas?

Exercise:**Problem:**

Four moles of a monatomic ideal gas in a cylinder at 27°C is expanded at constant pressure equal to 1 atm until its volume doubles. (a) What is the change in internal energy? (b) How much work was done by the gas in the process? (c) How much heat was transferred to the gas?

Solution:

a. 15,000 J; b. 10,000 J; c. 25,000 J

Exercise:**Problem:**

Helium gas is cooled from 20°C to 10°C by expanding from 40 atm to 1 atm. If there is 1.4 mol of helium, (a) What is the final volume of helium? (b) What is the change in internal energy?

Exercise:**Problem:**

In an adiabatic process, oxygen gas in a container is compressed along a path that can be described by the following pressure in atm as a function of volume V , with $V_0 = 1\text{ L}$: $p = (3.0 \text{ atm})(V/V_0)^{-1.2}$. The initial and final volumes during the process were 2 L and 1.5 L, respectively. Find the amount of work done on the gas.

Solution:

78 J

Exercise:**Problem:**

A cylinder containing three moles of a monatomic ideal gas is heated at a constant pressure of 2 atm. The temperature of the gas changes from 300 K to 350 K as a result of the expansion. Find work done (a) on the gas; and (b) by the gas.

Exercise:**Problem:**

A cylinder containing three moles of nitrogen gas is heated at a constant pressure of 2 atm. The temperature of the gas changes from 300 K to 350 K as a result of the expansion. Find work done (a) on the gas, and (b) by the gas by using van der Waals equation of state instead of ideal gas law.

Solution:

A cylinder containing three moles of nitrogen gas is heated at a constant pressure of 2 atm. a. -1220 J; b. $+1220$ J

Exercise:**Problem:**

Two moles of a monatomic ideal gas such as oxygen is compressed adiabatically and reversibly from a state (3 atm, 5 L) to a state with a pressure of 4 atm. (a) Find the volume and temperature of the final state. (b) Find the temperature of the initial state. (c) Find work done by the gas in the process. (d) Find the change in internal energy in the process. Assume $C_V = 5R$ and $C_p = C_V + R$ for the diatomic ideal gas in the conditions given.

Exercise:

Problem:

An insulated vessel contains 1.5 moles of argon at 2 atm. The gas initially occupies a volume of 5 L. As a result of the adiabatic expansion the pressure of the gas is reduced to 1 atm. (a) Find the volume and temperature of the final state. (b) Find the temperature of the gas in the initial state. (c) Find the work done by the gas in the process. (d) Find the change in the internal energy of the gas in the process.

Solution:

a. 7.6 L, 61.6 K; b. 81.3 K; c. $3.63 \text{ L} \cdot \text{atm} = 367 \text{ J}$; d. -367 J

Challenge Problems**Exercise:****Problem:**

One mole of an ideal monatomic gas occupies a volume of $1.0 \times 10^{-2} \text{ m}^3$ at a pressure of $2.0 \times 10^5 \text{ N/m}^2$. (a) What is the temperature of the gas? (b) The gas undergoes a quasi-static adiabatic compression until its volume is decreased to $5.0 \times 10^{-3} \text{ m}^3$. What is the new gas temperature? (c) How much work is done on the gas during the compression? (d) What is the change in the internal energy of the gas?

Exercise:**Problem:**

One mole of an ideal gas is initially in a chamber of volume $1.0 \times 10^{-2} \text{ m}^3$ and at a temperature of 27°C . (a) How much heat is absorbed by the gas when it slowly expands isothermally to twice its initial volume? (b) Suppose the gas is slowly transformed to the same final state by first decreasing the pressure at constant volume and then expanding it isobarically. What is the heat transferred for this case? (c) Calculate the heat transferred when the gas is transformed quasi-statically to the same final state by expanding it isobarically, then decreasing its pressure at constant volume.

Solution:

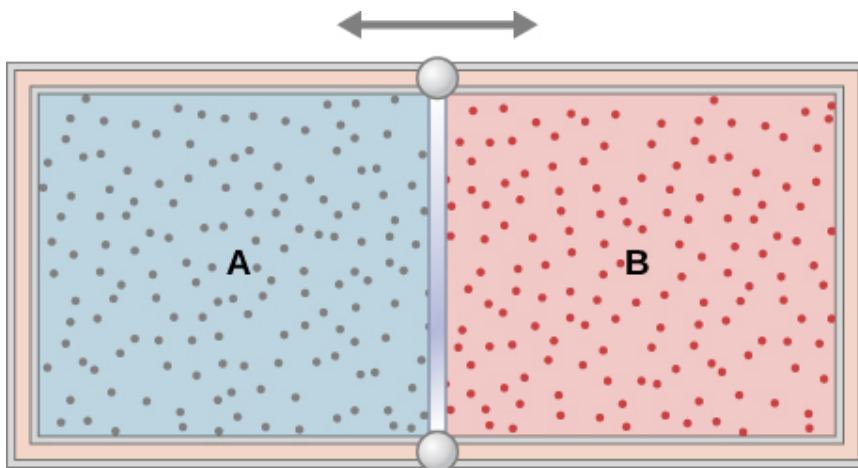
a. 1700 J; b. 1200 J; c. 2400 J

Exercise:**Problem:**

A bullet of mass 10 g is traveling horizontally at 200 m/s when it strikes and embeds in a pendulum bob of mass 2.0 kg. (a) How much mechanical energy is dissipated in the collision? (b) Assuming that C_v for the bob plus bullet is $3R$, calculate the temperature increase of the system due to the collision. Take the molecular mass of the system to be 200 g/mol.

Exercise:**Problem:**

The insulated cylinder shown below is closed at both ends and contains an insulating piston that is free to move on frictionless bearings. The piston divides the chamber into two compartments containing gases A and B. Originally, each compartment has a volume of $5.0 \times 10^{-2} \text{ m}^3$ and contains a monatomic ideal gas at a temperature of 0°C and a pressure of 1.0 atm. (a) How many moles of gas are in each compartment? (b) Heat Q is slowly added to A so that it expands and B is compressed until the pressure of both gases is 3.0 atm. Use the fact that the compression of B is adiabatic to determine the final volume of both gases. (c) What are their final temperatures? (d) What is the value of Q ?



Solution:

a. 2.2 mol; b. $V_A = 2.6 \times 10^{-2} \text{ m}^3$, $V_B = 7.4 \times 10^{-2} \text{ m}^3$; c. $T_A = 1220 \text{ K}$, $T_B = 430 \text{ K}$; d. 30,500 J

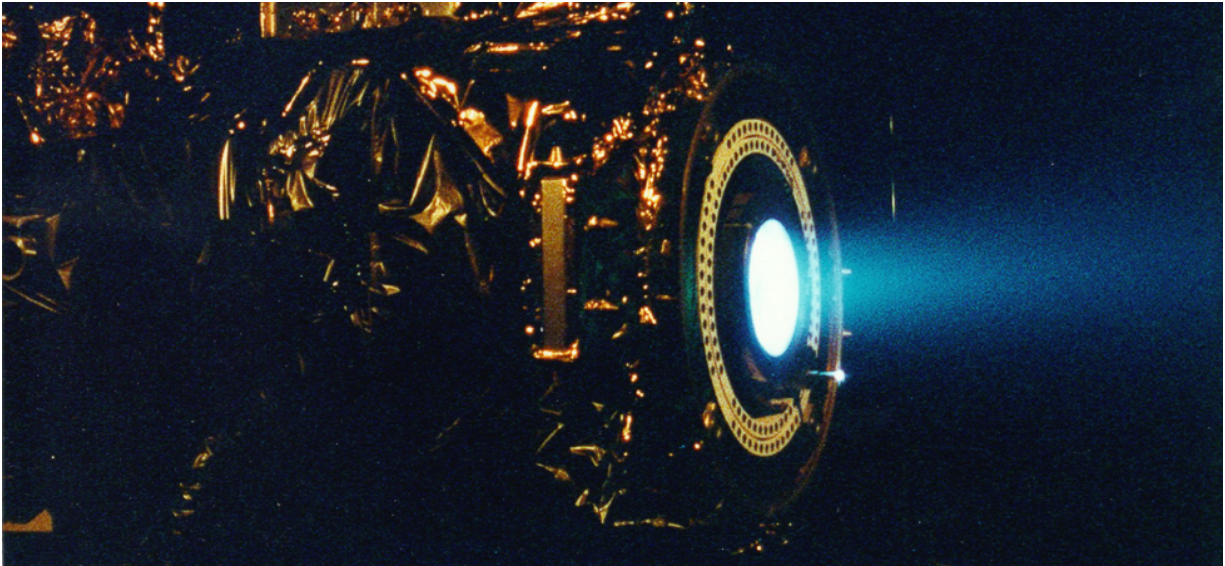
Exercise:**Problem:**

In a diesel engine, the fuel is ignited without a spark plug. Instead, air in a cylinder is compressed adiabatically to a temperature above the ignition temperature of the fuel; at the point of maximum compression, the fuel is injected into the cylinder. Suppose that air at 20°C is taken into the cylinder at a volume V_1 and then compressed adiabatically and quasi-statically to a temperature of 600°C and a volume V_2 . If $\gamma = 1.4$, what is the ratio V_1/V_2 ? (Note: In an operating diesel engine, the compression is not quasi-static.)

Introduction

class="introduction"

A xenon ion engine from the Jet Propulsion Laboratory shows the faint blue glow of charged atoms emitted from the engine. The ion propulsion engine is the first nonchemical propulsion to be used as the primary means of propelling a spacecraft. (credit: modification of work by NASA/JPL)



According to the first law of thermodynamics, the only processes that can occur are those that conserve energy. But this cannot be the only restriction imposed by nature, because many seemingly possible thermodynamic processes that would conserve energy do not occur. For example, when two bodies are in thermal contact, heat never flows from the colder body to the warmer one, even though this is not forbidden by the first law. So some other thermodynamic principles must be controlling the behavior of physical systems.

One such principle is the *second law of thermodynamics*, which limits the use of energy within a source. Energy cannot arbitrarily pass from one object to another, just as we cannot transfer heat from a cold object to a hot one without doing any work. We cannot unmix cream from coffee without a chemical process that changes the physical characteristics of the system or its environment. We cannot use internal energy stored in the air to propel a car, or use the energy of the ocean to run a ship, without disturbing something around that object.

In the chapter covering the first law of thermodynamics, we started our discussion with a joke by C. P. Snow stating that the first law means “you can’t win.” He paraphrased the second law as “you can’t break even, except on a very cold day.” Unless you are at zero kelvin, you cannot convert 100% of thermal energy into work. We start by discussing spontaneous

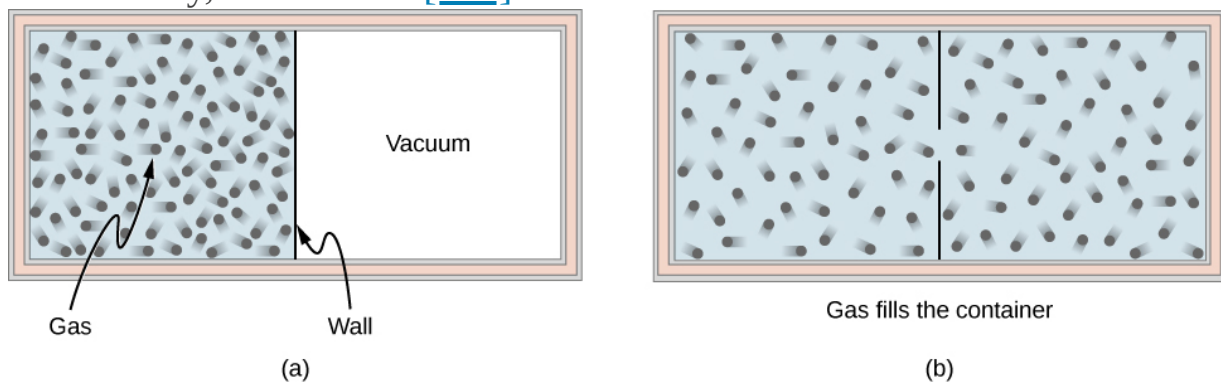
processes and explain why some processes require work to occur even if energy would have been conserved.

Reversible and Irreversible Processes

By the end of this section, you will be able to:

- Define reversible and irreversible processes
- State the second law of thermodynamics via an irreversible process

Consider an ideal gas that is held in half of a thermally insulated container by a wall in the middle of the container. The other half of the container is under vacuum with no molecules inside. Now, if we remove the wall in the middle quickly, the gas expands and fills up the entire container immediately, as shown in [\[link\]](#).



A gas expanding from half of a container to the entire container (a) before and (b) after the wall in the middle is removed.

Because half of the container is under vacuum before the gas expands there, we do not expect any work to be done by the system—that is, $W = 0$ —because no force from the vacuum is exerted on the gas during the expansion. If the container is thermally insulated from the rest of the environment, we do not expect any heat transfer to the system either, so $Q = 0$. Then the first law of thermodynamics leads to the change of the internal energy of the system,

Equation:

$$\Delta E_{\text{int}} = Q - W = 0.$$

For an ideal gas, if the internal energy doesn't change, then the temperature stays the same. Thus, the equation of state of the ideal gas gives us the final pressure of the gas, $p = nRT/V = p_0/2$, where p_0 is the pressure of the gas before the expansion. The volume is doubled and the pressure is halved, but nothing else seems to have changed during the expansion.

All of this discussion is based on what we have learned so far and makes sense. Here is what puzzles us: Can all the molecules go backward to the original half of the container in some future time? Our intuition tells us that this is going to be very unlikely, even though nothing we have learned so far prevents such an event from happening, regardless of how small the probability is. What we are really asking is whether the expansion into the vacuum half of the container is *reversible*.

A **reversible process** is a process in which the system and environment can be restored to exactly the same initial states that they were in before the process occurred, if we go backward along the path of the process. The necessary condition for a reversible process is therefore the quasi-static requirement. Note that it is quite easy to restore a system to its original state; the hard part is to have its environment restored to its original state at the same time. For example, in the example of an ideal gas expanding into vacuum to twice its original volume, we can easily push it back with a piston and restore its temperature and pressure by removing some heat from the gas. The problem is that we cannot do it without changing something in its surroundings, such as dumping some heat there.

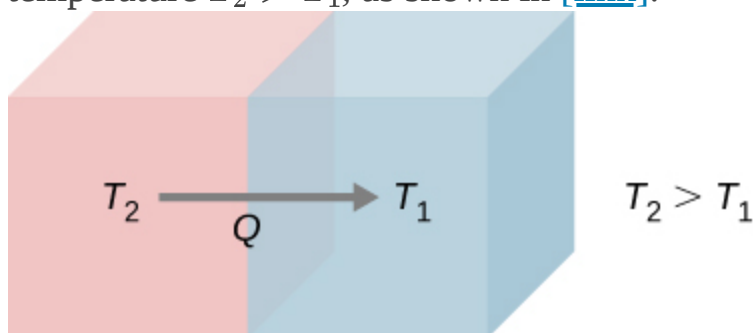
A reversible process is truly an ideal process that rarely happens. We can make certain processes close to reversible and therefore use the consequences of the corresponding reversible processes as a starting point or reference. In reality, almost all processes are irreversible, and some properties of the environment are altered when the properties of the system are restored. The expansion of an ideal gas, as we have just outlined, is irreversible because the process is not even quasi-static, that is, not in an equilibrium state at any moment of the expansion.

From the microscopic point of view, a particle described by Newton's second law can go backward if we flip the direction of time. But this is not

the case, in practical terms, in a macroscopic system with more than 10^{23} particles or molecules, where numerous collisions between these molecules tend to erase any trace of memory of the initial trajectory of each of the particles. For example, we can actually estimate the chance for all the particles in the expanded gas to go back to the original half of the container, but the current age of the universe is still not long enough for it to happen even once.

An **irreversible process** is what we encounter in reality almost all the time. The system and its environment cannot be restored to their original states at the same time. Because this is what happens in nature, it is also called a natural process. The sign of an irreversible process comes from the finite gradient between the states occurring in the actual process. For example, when heat flows from one object to another, there is a finite temperature difference (gradient) between the two objects. More importantly, at any given moment of the process, the system most likely is not at equilibrium or in a well-defined state. This phenomenon is called **irreversibility**.

Let us see another example of irreversibility in thermal processes. Consider two objects in thermal contact: one at temperature T_1 and the other at temperature $T_2 > T_1$, as shown in [\[link\]](#).



Spontaneous heat flow from an object at higher temperature T_2 to another at lower temperature T_1 .

We know from common personal experience that heat flows from a hotter object to a colder one. For example, when we hold a few pieces of ice in

our hands, we feel cold because heat has left our hands into the ice. The opposite is true when we hold one end of a metal rod while keeping the other end over a fire. Based on all of the experiments that have been done on spontaneous heat transfer, the following statement summarizes the governing principle:

Note:

Second Law of Thermodynamics (Clausius statement)

Heat never flows spontaneously from a colder object to a hotter object.

This statement turns out to be one of several different ways of stating the second law of thermodynamics. The form of this statement is credited to German physicist Rudolf Clausius (1822–1888) and is referred to as the **Clausius statement of the second law of thermodynamics**. The word “spontaneously” here means no other effort has been made by a third party, or one that is neither the hotter nor colder object. We will introduce some other major statements of the second law and show that they imply each other. In fact, all the different statements of the second law of thermodynamics can be shown to be equivalent, and all lead to the irreversibility of spontaneous heat flow between macroscopic objects of a very large number of molecules or particles.

Both isothermal and adiabatic processes sketched on a pV graph (discussed in [The First Law of Thermodynamics](#)) are reversible in principle because the system is always at an equilibrium state at any point of the processes and can go forward or backward along the given curves. Other idealized processes can be represented by pV curves; [\[link\]](#) summarizes the most common reversible processes.

Process	Constant Quantity and Resulting Fact
Isobaric	Constant pressure $W = p\Delta V$
Isochoric	Constant volume $W = 0$
Isothermal	Constant temperature $\Delta T = 0$
Adiabatic	No heat transfer $Q = 0$

Summary of Simple Thermodynamic Processes

Summary

- A reversible process is one in which both the system and its environment can return to exactly the states they were in by following the reverse path.
- An irreversible process is one in which the system and its environment cannot return together to exactly the states that they were in.
- The irreversibility of any natural process results from the second law of thermodynamics.

Conceptual Questions

Exercise:

Problem:

State an example of a process that occurs in nature that is as close to reversible as it can be.

Solution:

Some possible solutions are frictionless movement; restrained compression or expansion; energy transfer as heat due to infinitesimal temperature nonuniformity; electric current flow through a zero

resistance; restrained chemical reaction; and mixing of two samples of the same substance at the same state.

Problems

Exercise:

Problem:

A tank contains 111.0 g chlorine gas (Cl_2), which is at temperature 82.0°C and absolute pressure $5.70 \times 10^5 \text{ Pa}$. The temperature of the air outside the tank is 20.0°C . The molar mass of Cl_2 is 70.9 g/mol. (a) What is the volume of the tank? (b) What is the internal energy of the gas? (c) What is the work done by the gas if the temperature and pressure inside the tank drop to 31.0°C and $3.80 \times 10^5 \text{ Pa}$, respectively, due to a leak?

Exercise:

Problem:

A mole of ideal monatomic gas at 0°C and 1.00 atm is warmed up to expand isobarically to triple its volume. How much heat is transferred during the process?

Solution:

$$4.53 \times 10^3 \text{ J}$$

Exercise:

Problem:

A mole of an ideal gas at pressure 4.00 atm and temperature 298 K expands isothermally to double its volume. What is the work done by the gas?

Exercise:

Problem:

After a free expansion to quadruple its volume, a mole of ideal diatomic gas is compressed back to its original volume isobarically and then cooled down to its original temperature. What is the minimum heat removed from the gas in the final step to restoring its state?

Solution:

$$4.5 pV_0$$

Glossary

Clausius statement of the second law of thermodynamics

heat never flows spontaneously from a colder object to a hotter object

irreversibility

phenomenon associated with a natural process

irreversible process

process in which neither the system nor its environment can be restored to their original states at the same time

reversible process

process in which both the system and the external environment theoretically can be returned to their original states

Heat Engines

By the end of this section, you will be able to:

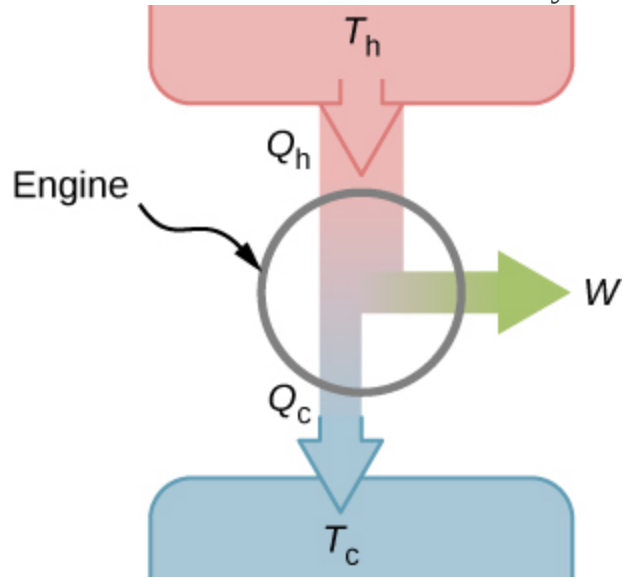
- Describe the function and components of a heat engine
- Explain the efficiency of an engine
- Calculate the efficiency of an engine for a given cycle of an ideal gas

A **heat engine** is a device used to extract heat from a source and then convert it into mechanical work that is used for all sorts of applications. For example, a steam engine on an old-style train can produce the work needed for driving the train. Several questions emerge from the construction and application of heat engines. For example, what is the maximum percentage of the heat extracted that can be used to do work? This turns out to be a question that can only be answered through the second law of thermodynamics.

The second law of thermodynamics can be formally stated in several ways. One statement presented so far is about the direction of spontaneous heat flow, known as the Clausius statement. A couple of other statements are based on heat engines. *Whenever we consider heat engines and associated devices such as refrigerators and heat pumps, we do not use the normal sign convention for heat and work.* For convenience, we assume that the symbols Q_h , Q_c , and W represent only the amounts of heat transferred and work delivered, regardless what the givers or receivers are. Whether heat is entering or leaving a system and work is done to or by a system are indicated by proper signs in front of the symbols and by the directions of arrows in diagrams.

It turns out that we need more than one heat source/sink to construct a heat engine. We will come back to this point later in the chapter, when we compare different statements of the second law of thermodynamics. For the moment, we assume that a heat engine is constructed between a heat source (high-temperature reservoir or hot reservoir) and a heat sink (low-temperature reservoir or cold reservoir), represented schematically in [\[link\]](#). The engine absorbs heat Q_h from a heat source (**hot reservoir**) of Kelvin temperature T_h , uses some of that energy to produce useful work W , and then discards the remaining energy as heat Q_c into a heat sink (**cold reservoir**) of Kelvin temperature T_c . Power plants and internal combustion

engines are examples of heat engines. Power plants use steam produced at high temperature to drive electric generators, while exhausting heat to the atmosphere or a nearby body of water in the role of the heat sink. In an internal combustion engine, a hot gas-air mixture is used to push a piston, and heat is exhausted to the nearby atmosphere in a similar manner.



A schematic representation of a heat engine. Energy flows from the hot reservoir to the cold reservoir while doing work.

Actual heat engines have many different designs. Examples include internal combustion engines, such as those used in most cars today, and external combustion engines, such as the steam engines used in old steam-engine trains. [\[link\]](#) shows a photo of a nuclear power plant in operation. The atmosphere around the reactors acts as the cold reservoir, and the heat generated from the nuclear reaction provides the heat from the hot reservoir.



The heat exhausted from a nuclear power plant goes to the cooling towers, where it is released into the atmosphere.

Heat engines operate by carrying a *working substance* through a cycle. In a steam power plant, the working substance is water, which starts as a liquid, becomes vaporized, is then used to drive a turbine, and is finally condensed back into the liquid state. As is the case for all working substances in cyclic processes, once the water returns to its initial state, it repeats the same sequence.

For now, we assume that the cycles of heat engines are reversible, so there is no energy loss to friction or other irreversible effects. Suppose that the engine of [\[link\]](#) goes through one complete cycle and that Q_h , Q_c , and W represent the heats exchanged and the work done for that cycle. Since the initial and final states of the system are the same, $\Delta E_{\text{int}} = 0$ for the cycle. We therefore have from the first law of thermodynamics,

Equation:

$$W = Q - \Delta E_{\text{int}} = (Q_h - Q_c) - 0,$$

so that

Note:

Equation:

$$W = Q_h - Q_c.$$

The most important measure of a heat engine is its **efficiency (e)**, which is simply “what we get out” divided by “what we put in” during each cycle, as defined by $e = W_{\text{out}}/Q_{\text{in}}$.

With a heat engine working between two heat reservoirs, we get out W and put in Q_h , so the efficiency of the engine is

Note:

Equation:

$$e = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h}.$$

Here, we used [\[link\]](#), $W = Q_h - Q_c$, in the final step of this expression for the efficiency.

Example:

A Lawn Mower

A lawn mower is rated to have an efficiency of 25.0% and an average power of 3.00 kW. What are (a) the average work and (b) the minimum heat discharge into the air by the lawn mower in one minute of use?

Strategy

From the average power—that is, the rate of work production—we can figure out the work done in the given elapsed time. Then, from the

efficiency given, we can figure out the minimum heat discharge $Q_c = Q_h(1 - e)$ with $Q_h = Q_c + W$.

Solution

- a. The average work delivered by the lawn mower is

Equation:

$$W = P\Delta t = 3.00 \times 10^3 \times 60 \times 1.00 \text{ J} = 180 \text{ kJ}.$$

- b. The minimum heat discharged into the air is given by

Equation:

$$Q_c = Q_h(1 - e) = (Q_c + W)(1 - e),$$

which leads to

Equation:

$$Q_c = W(1/e - 1) = 180 \times (1/0.25 - 1) \text{ kJ} = 540 \text{ kJ}.$$

Significance

As the efficiency rises, the minimum heat discharged falls. This helps our environment and atmosphere by not having as much waste heat expelled.

Summary

- The work done by a heat engine is the difference between the heat absorbed from the hot reservoir and the heat discharged to the cold reservoir, that is, $W = Q_h - Q_c$.
- The ratio of the work done by the engine and the heat absorbed from the hot reservoir provides the efficiency of the engine, that is, $e = W/Q_h = 1 - Q_c/Q_h$.

Conceptual Questions

Exercise:**Problem:**

Explain in practical terms why efficiency is defined as W/Q_h .

Problems**Exercise:****Problem:**

An engine is found to have an efficiency of 0.40. If it does 200 J of work per cycle, what are the corresponding quantities of heat absorbed and discharged?

Exercise:**Problem:**

In performing 100.0 J of work, an engine discharges 50.0 J of heat. What is the efficiency of the engine?

Solution:

0.667

Exercise:**Problem:**

An engine with an efficiency of 0.30 absorbs 500 J of heat per cycle. (a) How much work does it perform per cycle? (b) How much heat does it discharge per cycle?

Exercise:**Problem:**

It is found that an engine discharges 100.0 J while absorbing 125.0 J each cycle of operation. (a) What is the efficiency of the engine? (b) How much work does it perform per cycle?

Solution:

a. 0.556; b. 125.0 J

Exercise:**Problem:**

The temperature of the cold reservoir of the engine is 300 K. It has an efficiency of 0.30 and absorbs 500 J of heat per cycle. (a) How much work does it perform per cycle? (b) How much heat does it discharge per cycle?

Exercise:**Problem:**

An engine absorbs three times as much heat as it discharges. The work done by the engine per cycle is 50 J. Calculate (a) the efficiency of the engine, (b) the heat absorbed per cycle, and (c) the heat discharged per cycle.

Solution:

a. 0.50; b. 100 J; c. 50 J

Exercise:**Problem:**

A coal power plant consumes 100,000 kg of coal per hour and produces 500 MW of power. If the heat of combustion of coal is 30 MJ/kg, what is the efficiency of the power plant?

Glossary

cold reservoir

sink of heat used by a heat engine

efficiency (e)

output work from the engine over the input heat to the engine from the hot reservoir

heat engine

device that converts heat into work

hot reservoir

source of heat used by a heat engine

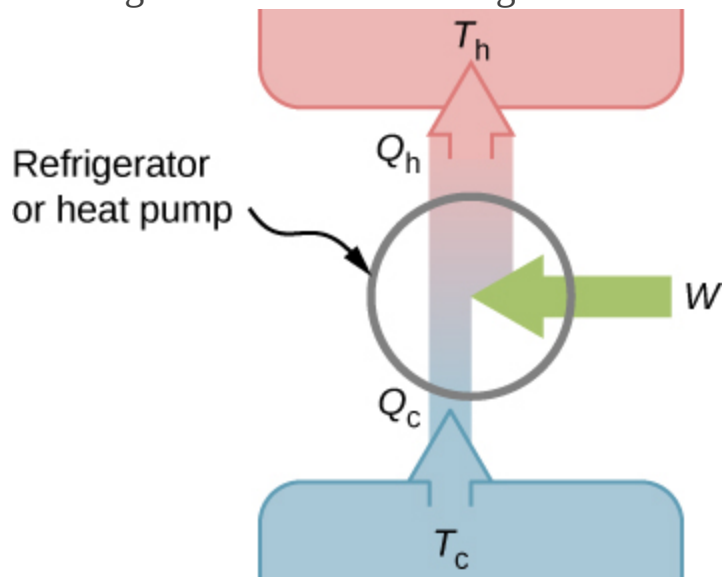
Refrigerators and Heat Pumps

By the end of this section, you will be able to:

- Describe a refrigerator and a heat pump and list their differences
- Calculate the performance coefficients of simple refrigerators and heat pumps

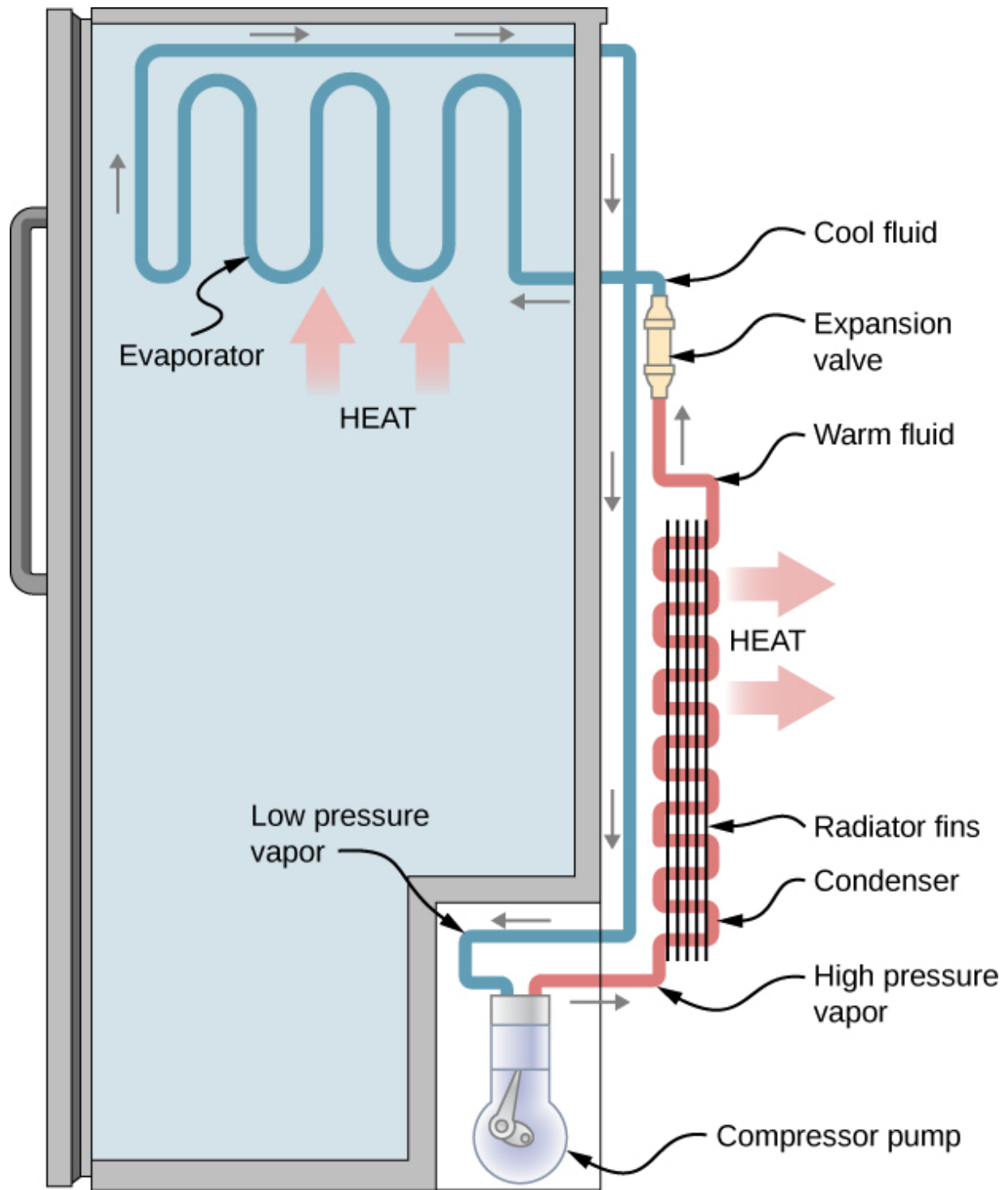
The cycles we used to describe the engine in the preceding section are all reversible, so each sequence of steps can just as easily be performed in the opposite direction. In this case, the engine is known as a refrigerator or a heat pump, depending on what is the focus: the heat removed from the cold reservoir or the heat dumped to the hot reservoir. Either a refrigerator or a heat pump is an engine running in reverse. For a **refrigerator**, the focus is on removing heat from a specific area. For a **heat pump**, the focus is on dumping heat to a specific area.

We first consider a refrigerator ([\[link\]](#)). The purpose of this engine is to remove heat from the cold reservoir, which is the space inside the refrigerator for an actual household refrigerator or the space inside a building for an air-conditioning unit.



A schematic representation of a refrigerator (or a heat pump). The arrow next to work (W) indicates work being put into the system.

A refrigerator (or heat pump) absorbs heat Q_c from the cold reservoir at Kelvin temperature T_c and discards heat Q_h to the hot reservoir at Kelvin temperature T_h , while work W is done on the engine's working substance, as shown by the arrow pointing toward the system in the figure. A household refrigerator removes heat from the food within it while exhausting heat to the surrounding air. The required work, for which we pay in our electricity bill, is performed by the motor that moves a coolant through the coils. A schematic sketch of a household refrigerator is given in [\[link\]](#).



A schematic diagram of a household refrigerator. A coolant with a boiling temperature below the freezing point of water is sent through the cycle (clockwise in this diagram). The coolant extracts heat from the refrigerator at the evaporator, causing coolant to vaporize. It is then

compressed and sent through the condenser, where it exhausts heat to the outside.

The effectiveness or **coefficient of performance** K_R of a refrigerator is measured by the heat removed from the cold reservoir divided by the work done by the working substance cycle by cycle:

Note:

Equation:

$$K_R = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c}.$$

Note that we have used the condition of energy conservation, $W = Q_h - Q_c$, in the final step of this expression.

The effectiveness or coefficient of performance K_P of a heat pump is measured by the heat dumped to the hot reservoir divided by the work done to the engine on the working substance cycle by cycle:

Note:

Equation:

$$K_P = \frac{Q_h}{W} = \frac{Q_h}{Q_h - Q_c}.$$

Once again, we use the energy conservation condition $W = Q_h - Q_c$ to obtain the final step of this expression.

Summary

- A refrigerator or a heat pump is a heat engine run in reverse.
- The focus of a refrigerator is on removing heat from the cold reservoir with a coefficient of performance K_R .
- The focus of a heat pump is on dumping heat to the hot reservoir with a coefficient of performance K_P .

Conceptual Questions

Exercise:

Problem:

If the refrigerator door is left open, what happens to the temperature of the kitchen?

Solution:

The temperature increases since the heat output behind the refrigerator is greater than the cooling from the inside of the refrigerator.

Exercise:

Problem:

Is it possible for the efficiency of a reversible engine to be greater than 1.0? Is it possible for the coefficient of performance of a reversible refrigerator to be less than 1.0?

Problems

Exercise:

Problem:

A refrigerator has a coefficient of performance of 3.0. (a) If it requires 200 J of work per cycle, how much heat per cycle does it remove the cold reservoir? (b) How much heat per cycle is discarded to the hot reservoir?

Solution:

a. 600 J; b. 800 J

Exercise:**Problem:**

During one cycle, a refrigerator removes 500 J from a cold reservoir and discharges 800 J to its hot reservoir. (a) What is its coefficient of performance? (b) How much work per cycle does it require to operate?

Exercise:**Problem:**

If a refrigerator discards 80 J of heat per cycle and its coefficient of performance is 6.0, what are (a) the quantity of heat it removes per cycle from a cold reservoir and (b) the amount of work per cycle required for its operation?

Solution:

a. 69 J; b. 11 J

Exercise:**Problem:**

A refrigerator has a coefficient of performance of 3.0. (a) If it requires 200 J of work per cycle, how much heat per cycle does it remove the cold reservoir? (b) How much heat per cycle is discarded to the hot reservoir?

Glossary

coefficient of performance

measure of effectiveness of a refrigerator or heat pump

heat pump

device that delivers heat to a hot reservoir

refrigerator

device that removes heat from a cold reservoir

Statements of the Second Law of Thermodynamics

By the end of this section, you will be able to:

- Contrast the second law of thermodynamics statements according to Kelvin and Clausius formulations
- Interpret the second of thermodynamics via irreversibility

Earlier in this chapter, we introduced the Clausius statement of the second law of thermodynamics, which is based on the irreversibility of spontaneous heat flow. As we remarked then, the second law of thermodynamics can be stated in several different ways, and all of them can be shown to imply the others. In terms of heat engines, the second law of thermodynamics may be stated as follows:

Note:

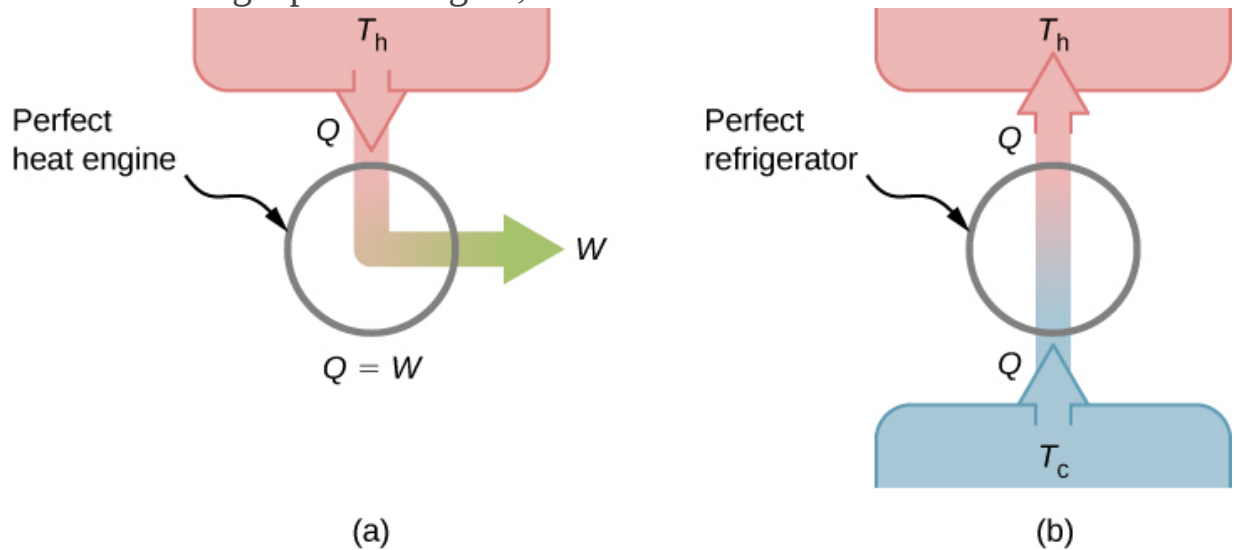
Second Law of Thermodynamics (Kelvin statement)

It is impossible to convert the heat from a single source into work without any other effect.

This is known as the **Kelvin statement of the second law of thermodynamics**. This statement describes an unattainable “**perfect engine**,” as represented schematically in [\[link\]\(a\)](#). Note that “without any other effect” is a very strong restriction. For example, an engine can absorb heat and turn it all into work, *but not if it completes a cycle*. Without completing a cycle, the substance in the engine is not in its original state and therefore an “other effect” has occurred. Another example is a chamber of gas that can absorb heat from a heat reservoir and do work isothermally against a piston as it expands. However, if the gas were returned to its initial state (that is, made to complete a cycle), it would have to be compressed and heat would have to be extracted from it.

The Kelvin statement is a manifestation of a well-known engineering problem. Despite advancing technology, we are not able to build a heat

engine that is 100% efficient. The first law does not exclude the possibility of constructing a perfect engine, but the second law forbids it.



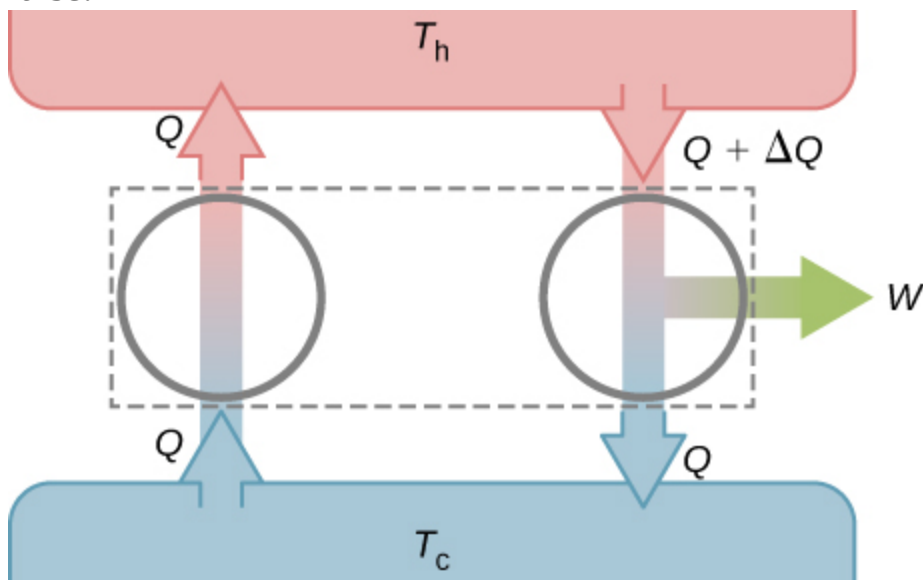
(a) A “perfect heat engine” converts all input heat into work. (b) A “perfect refrigerator” transports heat from a cold reservoir to a hot reservoir without work input. Neither of these devices is achievable in reality.

We can show that the Kelvin statement is equivalent to the Clausius statement if we view the two objects in the Clausius statement as a cold reservoir and a hot reservoir. Thus, the Clausius statement becomes: *It is impossible to construct a refrigerator that transfers heat from a cold reservoir to a hot reservoir without aid from an external source.* The Clausius statement is related to the everyday observation that heat never flows spontaneously from a cold object to a hot object. *Heat transfer in the direction of increasing temperature always requires some energy input.* A “**perfect refrigerator**,” shown in [\[link\]](#)(b), which works without such external aid, is impossible to construct.

To prove the equivalence of the Kelvin and Clausius statements, we show that if one statement is false, it necessarily follows that the other statement is also false. Let us first assume that the Clausius statement is false, so that the perfect refrigerator of [\[link\]](#)(b) does exist. The refrigerator removes heat

Q from a cold reservoir at a temperature T_c and transfers all of it to a hot reservoir at a temperature T_h . Now consider a real heat engine working in the same temperature range. It extracts heat $Q + \Delta Q$ from the hot reservoir, does work W , and discards heat Q to the cold reservoir. From the first law, these quantities are related by $W = (Q + \Delta Q) - Q = \Delta Q$.

Suppose these two devices are combined as shown in [\[link\]](#). The net heat removed from the hot reservoir is ΔQ , no net heat transfer occurs to or from the cold reservoir, and work W is done on some external body. Since $W = \Delta Q$, the combination of a perfect refrigerator and a real heat engine is itself a perfect heat engine, thereby contradicting the Kelvin statement. Thus, if the Clausius statement is false, the Kelvin statement must also be false.

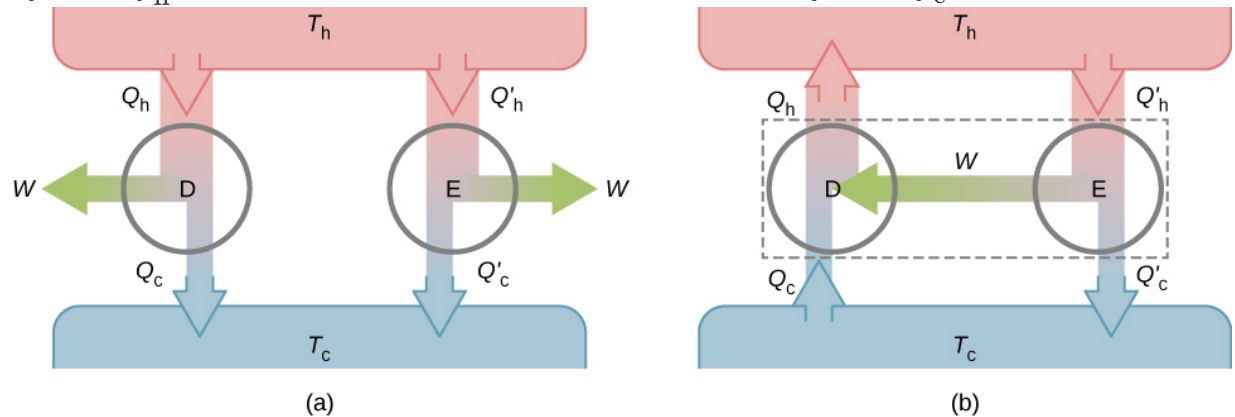


Combining a perfect refrigerator and a real heat engine yields a perfect heat engine because

$$W = \Delta Q.$$

Using the second law of thermodynamics, we now prove two important properties of heat engines operating between two heat reservoirs. The first property is that *any reversible engine operating between two reservoirs has a greater efficiency than any irreversible engine operating between the same two reservoirs.*

The second property to be demonstrated is that *all reversible engines operating between the same two reservoirs have the same efficiency*. To show this, we start with the two engines D and E of [\[link\]](#)(a), which are operating between two common heat reservoirs at temperatures T_h and T_c . First, we assume that D is a reversible engine and that E is a hypothetical irreversible engine that has a higher efficiency than D. If both engines perform the same amount of work W per cycle, it follows from [\[link\]](#) that $Q_h > Q'_h$. It then follows from the first law that $Q_c > Q'_c$.



(a) Two uncoupled engines D and E working between the same reservoirs. (b) The coupled engines, with D working in reverse.

Suppose the cycle of D is reversed so that it operates as a refrigerator, and the two engines are coupled such that the work output of E is used to drive D, as shown in [\[link\]](#)(b). Since $Q_h > Q'_h$ and $Q_c > Q'_c$, the net result of each cycle is equivalent to a spontaneous transfer of heat from the cold reservoir to the hot reservoir, a process the second law does not allow. The original assumption must therefore be wrong, and it is impossible to construct an irreversible engine such that E is more efficient than the reversible engine D.

Now it is quite easy to demonstrate that the efficiencies of all reversible engines operating between the same reservoirs are equal. Suppose that D and E are both reversible engines. If they are coupled as shown in [\[link\]](#)(b), the efficiency of E cannot be greater than the efficiency of D, or the second law would be violated. If both engines are then reversed, the same

reasoning implies that the efficiency of D cannot be greater than the efficiency of E. Combining these results leads to the conclusion that all reversible engines working between the same two reservoirs have the same efficiency.

Note:

Exercise:

Problem:

Check Your Understanding What is the efficiency of a perfect heat engine? What is the coefficient of performance of a perfect refrigerator?

Solution:

A perfect heat engine would have $Q_c = 0$, which would lead to $e = 1 - Q_c/Q_h = 1$. A perfect refrigerator would need zero work, that is, $W = 0$, which leads to $K_R = Q_c/W \rightarrow \infty$.

Note:

Exercise:

Problem:

Check Your Understanding Show that $Q_h - Q'_h = Q_c - Q'_c$ for the hypothetical engine of [\[link\]](#)(b).

Solution:

From the engine on the right, we have $W = Q'_h - Q'_c$. From the refrigerator on the right, we have $Q_h = Q_c + W$. Thus, $W = Q'_h - Q'_c = Q_h - Q_c$.

Summary

- The Kelvin statement of the second law of thermodynamics: It is impossible to convert the heat from a single source into work without any other effect.
- The Kelvin statement and Clausius statement of the second law of thermodynamics are equivalent.

Conceptual Questions

Exercise:

Problem:

In the text, we showed that if the Clausius statement is false, the Kelvin statement must also be false. Now show the reverse, such that if the Kelvin statement is false, it follows that the Clausius statement is false.

Solution:

If we combine a perfect engine and a real refrigerator with the engine converting heat Q from the hot reservoir into work $W = Q$ to drive the refrigerator, then the heat dumped to the hot reservoir by the refrigerator will be $W + \Delta Q$, resulting in a perfect refrigerator transferring heat ΔQ from the cold reservoir to hot reservoir without any other effect.

Exercise:

Problem:

Why don't we operate ocean liners by extracting heat from the ocean or operate airplanes by extracting heat from the atmosphere?

Exercise:

Problem:

Discuss the practical advantages and disadvantages of heat pumps and electric heating.

Solution:

Heat pumps can efficiently extract heat from the ground to heat on cooler days or pull heat out of the house on warmer days. The disadvantage of heat pumps are that they are more costly than alternatives, require maintenance, and will not work efficiently when temperature differences between the inside and outside are very large. Electric heating is much cheaper to purchase than a heat pump; however, it may be more costly to run depending on the electric rates and amount of usage.

Exercise:**Problem:**

The energy output of a heat pump is greater than the energy used to operate the pump. Why doesn't this statement violate the first law of thermodynamics?

Exercise:**Problem:**

Speculate as to why nuclear power plants are less efficient than fossil-fuel plants based on temperature arguments.

Solution:

A nuclear reactor needs to have a lower temperature to operate, so its efficiency will not be as great as a fossil-fuel plant. This argument does not take into consideration the amount of energy per reaction: Nuclear power has a far greater energy output than fossil fuels.

Exercise:

Problem:

An ideal gas goes from state (p_i, V_i) to state (p_f, V_f) when it is allowed to expand freely. Is it possible to represent the actual process on a pV diagram? Explain.

Glossary

Kelvin statement of the second law of thermodynamics

it is impossible to convert the heat from a single source into work without any other effect

perfect engine

engine that can convert heat into work with 100% efficiency

perfect refrigerator (heat pump)

refrigerator (heat pump) that can remove (dump) heat without any input of work

The Carnot Cycle

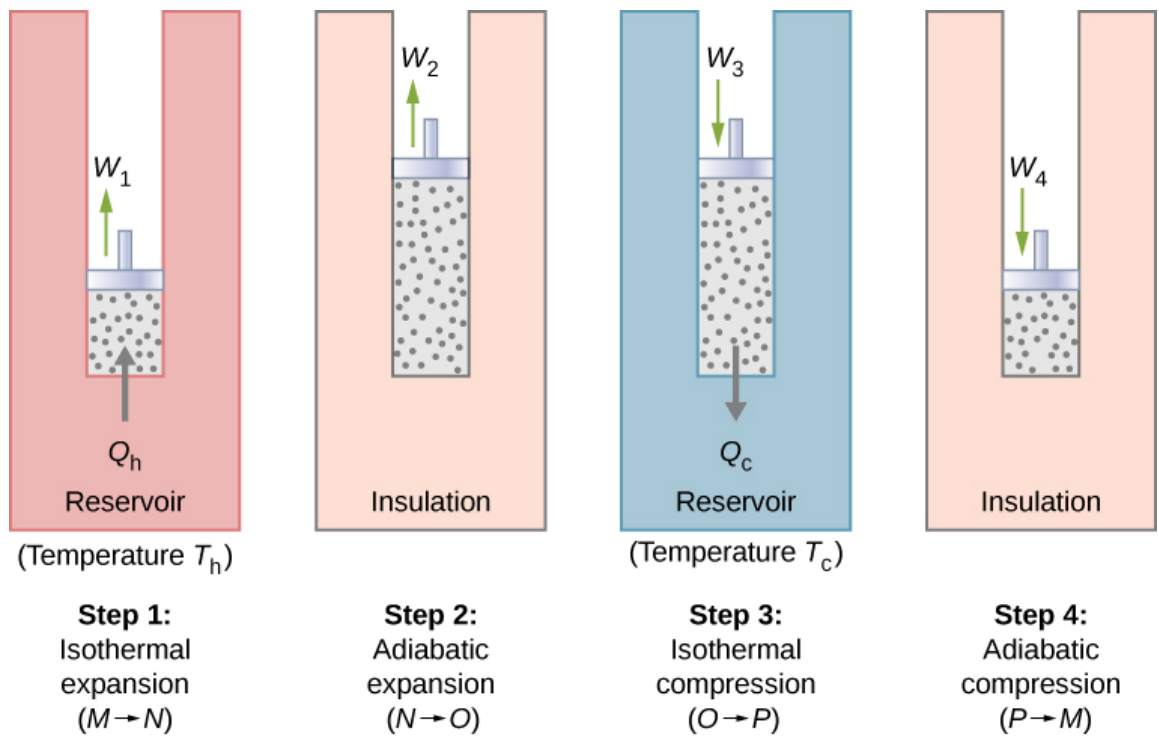
- Describe the Carnot cycle with the roles of all four processes involved
- Outline the Carnot principle and its implications
- Demonstrate the equivalence of the Carnot principle and the second law of thermodynamics

In the early 1820s, Sadi Carnot (1786–1832), a French engineer, became interested in improving the efficiencies of practical heat engines. In 1824, his studies led him to propose a hypothetical working cycle with the highest possible efficiency between the same two reservoirs, known now as the **Carnot cycle**. An engine operating in this cycle is called a **Carnot engine**. The Carnot cycle is of special importance for a variety of reasons. At a practical level, this cycle represents a reversible model for the steam power plant and the refrigerator or heat pump. Yet, it is also very important theoretically, for it plays a major role in the development of another important statement of the second law of thermodynamics. Finally, because only two reservoirs are involved in its operation, it can be used along with the second law of thermodynamics to define an absolute temperature scale that is truly independent of any substance used for temperature measurement.

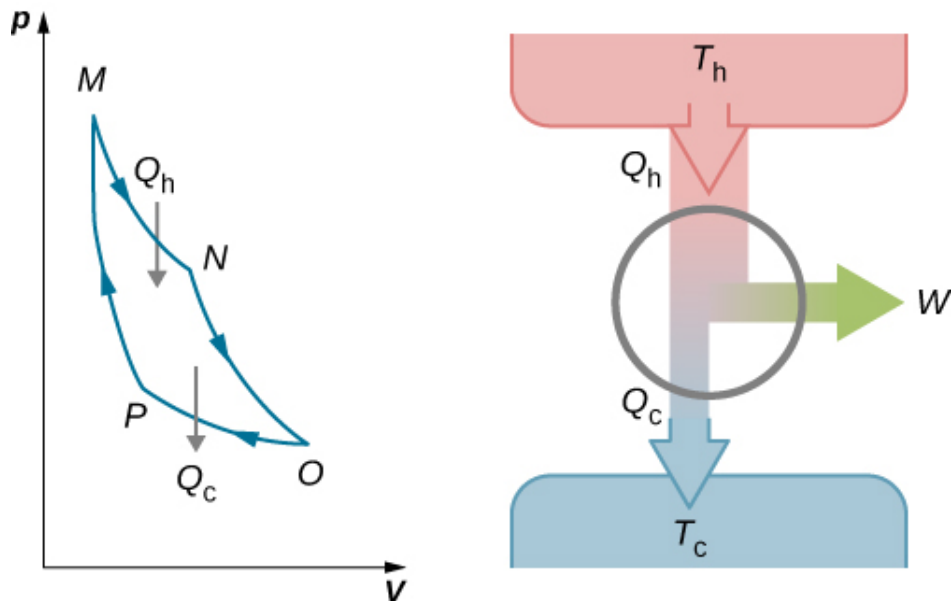
With an ideal gas as the working substance, the steps of the Carnot cycle, as represented by [\[link\]](#), are as follows.

1. *Isothermal expansion*. The gas is placed in thermal contact with a heat reservoir at a temperature T_h . The gas absorbs heat Q_h from the heat reservoir and is allowed to expand isothermally, doing work W_1 . Because the internal energy E_{int} of an ideal gas is a function of the temperature only, the change of the internal energy is zero, that is, $\Delta E_{\text{int}} = 0$ during this isothermal expansion. With the first law of thermodynamics, $\Delta E_{\text{int}} = Q - W$, we find that the heat absorbed by the gas is
Equation:

$$Q_h = W_1 = nRT_h \ln \frac{V_N}{V_M}.$$



The four processes of the Carnot cycle. The working substance is assumed to be an ideal gas whose thermodynamic path $MNOP$ is represented in [\[link\]](#).



The total work done by the gas in the Carnot cycle is

shown and given by the area enclosed by the loop
 $MNOPM$.

2. *Adiabatic expansion.* The gas is thermally isolated and allowed to expand further, doing work W_2 . Because this expansion is adiabatic, the temperature of the gas falls—in this case, from T_h to T_c . From $pV^\gamma = \text{constant}$ and the equation of state for an ideal gas, $pV = nRT$, we have

Equation:

$$TV^{\gamma-1} = \text{constant},$$

so that

Equation:

$$T_h V_N^{\gamma-1} = T_c V_O^{\gamma-1}.$$

3. *Isothermal compression.* The gas is placed in thermal contact with a cold reservoir at temperature T_c and compressed isothermally. During this process, work W_3 is done on the gas and it gives up heat Q_c to the cold reservoir. The reasoning used in step 1 now yields

Equation:

$$Q_c = nRT_c \ln \frac{V_O}{V_P},$$

where Q_c is the heat dumped to the cold reservoir by the gas.

4. *Adiabatic compression.* The gas is thermally isolated and returned to its initial state by compression. In this process, work W_4 is done on the gas. Because the compression is adiabatic, the temperature of the gas rises—from T_c to T_h in this particular case. The reasoning of step 2 now gives

Equation:

$$T_c V_P^{\gamma-1} = T_h V_M^{\gamma-1}.$$

The total work done by the gas in the Carnot cycle is given by

Equation:

$$W = W_1 + W_2 - W_3 - W_4.$$

This work is equal to the area enclosed by the loop shown in the pV diagram of [\[link\]](#). Because the initial and final states of the system are the same, the change of the internal energy of the gas in the cycle must be zero, that is, $\Delta E_{\text{int}} = 0$.

The first law of thermodynamics then gives

Equation:

$$W = Q - \Delta E_{\text{int}} = (Q_{\text{h}} - Q_{\text{c}}) - 0,$$

and

Equation:

$$W = Q_{\text{h}} - Q_{\text{c}}.$$

To find the efficiency of this engine, we first divide Q_{c} by Q_{h} :

Equation:

$$\frac{Q_{\text{c}}}{Q_{\text{h}}} = \frac{T_{\text{c}}}{T_{\text{h}}} \frac{\ln V_{\text{O}}/V_{\text{P}}}{\ln V_{\text{N}}/V_{\text{M}}}.$$

When the adiabatic constant from step 2 is divided by that of step 4, we find

Equation:

$$\frac{V_{\text{O}}}{V_{\text{P}}} = \frac{V_{\text{N}}}{V_{\text{M}}}.$$

Substituting this into the equation for $Q_{\text{c}}/Q_{\text{h}}$, we obtain

Equation:

$$\frac{Q_{\text{c}}}{Q_{\text{h}}} = \frac{T_{\text{c}}}{T_{\text{h}}}.$$

Finally, with [\[link\]](#), we find that the efficiency of this ideal gas Carnot engine is given by

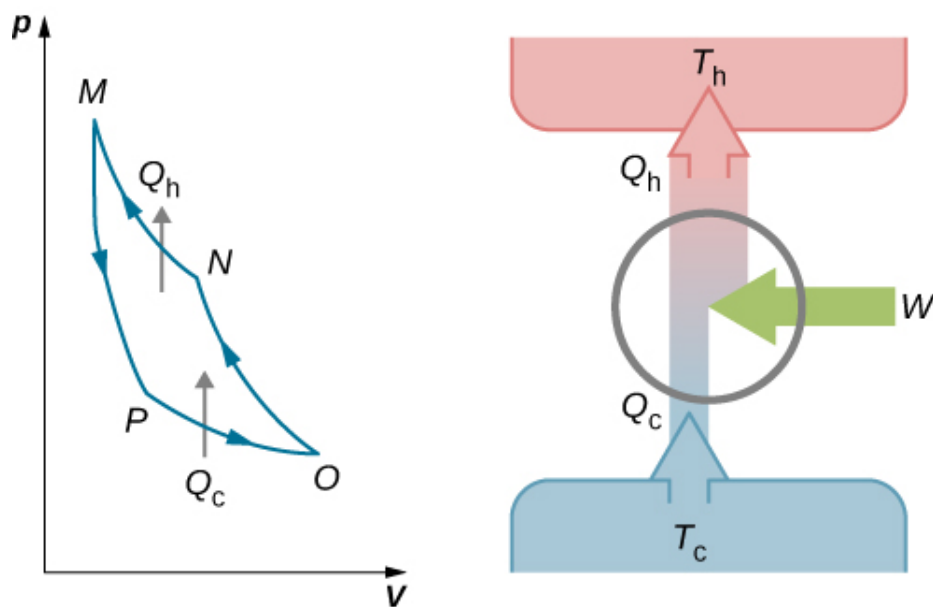
Note:

Equation:

$$e = 1 - \frac{T_c}{T_h}.$$

An engine does not necessarily have to follow a Carnot engine cycle. All engines, however, have the same *net* effect, namely the absorption of heat from a hot reservoir, the production of work, and the discarding of heat to a cold reservoir. This leads us to ask: Do all reversible cycles operating between the same two reservoirs have the same efficiency? The answer to this question comes from the second law of thermodynamics discussed earlier: *All reversible engine cycles produce exactly the same efficiency.* Also, as you might expect, all real engines operating between two reservoirs are less efficient than reversible engines operating between the same two reservoirs. This too is a consequence of the second law of thermodynamics shown earlier.

The cycle of an ideal gas Carnot refrigerator is represented by the pV diagram of [\[link\]](#). It is a Carnot engine operating in reverse. The refrigerator extracts heat Q_c from a cold-temperature reservoir at T_c when the ideal gas expands isothermally. The gas is then compressed adiabatically until its temperature reaches T_h , after which an isothermal compression of the gas results in heat Q_h being discarded to a high-temperature reservoir at T_h . Finally, the cycle is completed by an adiabatic expansion of the gas, causing its temperature to drop to T_c .



The work done on the gas in one cycle of the Carnot refrigerator is shown and given by the area enclosed by the loop *MPONM*.

The work done on the ideal gas is equal to the area enclosed by the path of the *pV* diagram. From the first law, this work is given by

Equation:

$$W = Q_h - Q_c.$$

An analysis just like the analysis done for the Carnot engine gives

Equation:

$$\frac{Q_c}{T_c} = \frac{Q_h}{T_h}.$$

When combined with [\[link\]](#), this yields

Note:

Equation:

$$K_R = \frac{T_c}{T_h - T_c}$$

for the coefficient of performance of the ideal-gas Carnot refrigerator. Similarly, we can work out the coefficient of performance for a Carnot heat pump as

Note:

Equation:

$$K_P = \frac{Q_h}{Q_h - Q_c} = \frac{T_h}{T_h - T_c}.$$

We have just found equations representing the efficiency of a Carnot engine and the coefficient of performance of a Carnot refrigerator or a Carnot heat pump, assuming an ideal gas for the working substance in both devices. However, these equations are more general than their derivations imply. We will soon show that they are both valid no matter what the working substance is.

Carnot summarized his study of the Carnot engine and Carnot cycle into what is now known as **Carnot's principle**:

Note:

Carnot's Principle

No engine working between two reservoirs at constant temperatures can have a greater efficiency than a reversible engine.

This principle can be viewed as another statement of the second law of thermodynamics and can be shown to be equivalent to the Kelvin statement and the Clausius statement.

Example:**The Carnot Engine**

A Carnot engine has an efficiency of 0.60 and the temperature of its cold reservoir is 300 K. (a) What is the temperature of the hot reservoir? (b) If the engine does 300 J of work per cycle, how much heat is removed from the high-temperature reservoir per cycle? (c) How much heat is exhausted to the low-temperature reservoir per cycle?

Strategy

From the temperature dependence of the thermal efficiency of the Carnot engine, we can find the temperature of the hot reservoir. Then, from the definition of the efficiency, we can find the heat removed when the work done by the engine is given. Finally, energy conservation will lead to how much heat must be dumped to the cold reservoir.

Solution

- a. From $e = 1 - T_c/T_h$ we have

Equation:

$$0.60 = 1 - \frac{300 \text{ K}}{T_h},$$

so that the temperature of the hot reservoir is

Equation:

$$T_h = \frac{300 \text{ K}}{1 - 0.60} = 750 \text{ K}.$$

- b. By definition, the efficiency of the engine is $e = W/Q$, so that the heat removed from the high-temperature reservoir per cycle is

Equation:

$$Q_h = \frac{W}{e} = \frac{300 \text{ J}}{0.60} = 500 \text{ J}.$$

- c. From the first law, the heat exhausted to the low-temperature reservoir per cycle by the engine is

Equation:

$$Q_c = Q_h - W = 500 \text{ J} - 300 \text{ J} = 200 \text{ J}.$$

Significance

A Carnot engine has the maximum possible efficiency of converting heat into work between two reservoirs, but this does not necessarily mean it is 100% efficient. As the difference in temperatures of the hot and cold reservoir increases, the efficiency of a Carnot engine increases.

Example:**A Carnot Heat Pump**

Imagine a Carnot heat pump operates between an outside temperature of $0\text{ }^{\circ}\text{C}$ and an inside temperature of $20.0\text{ }^{\circ}\text{C}$. What is the work needed if the heat delivered to the inside of the house is 30.0 kJ ?

Strategy

Because the heat pump is assumed to be a Carnot pump, its performance coefficient is given by $K_P = Q_h/W = T_h/(T_h - T_c)$. Thus, we can find the work W from the heat delivered Q_h .

Solution

The work needed is obtained from

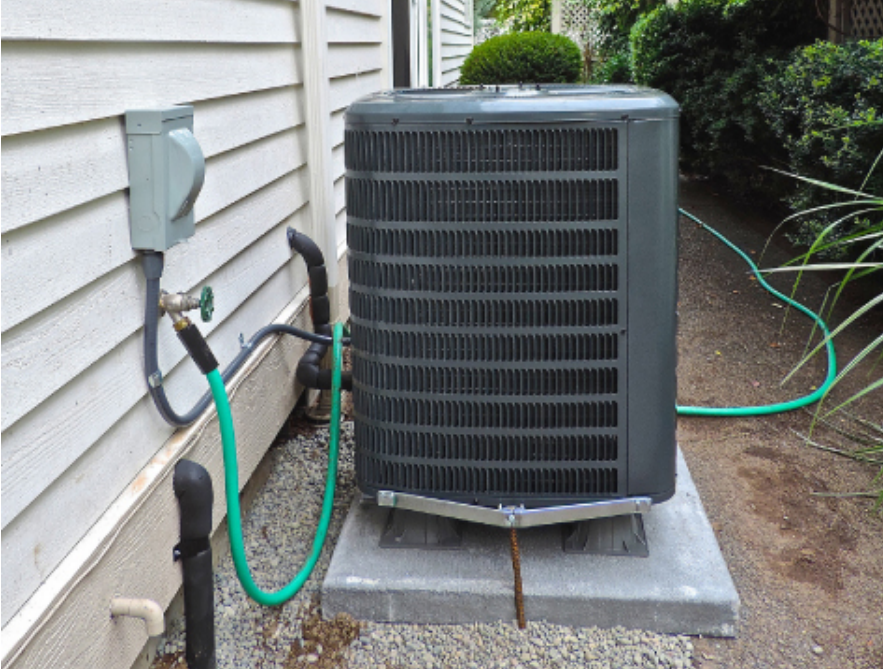
Equation:

$$W = Q_h/K_P = Q_h(T_h - T_c)/T_h = 30\text{ kJ} \times (293\text{ K} - 273\text{ K})/293\text{ K} = 2\text{ kJ}.$$

Significance

We note that this work depends not only on the heat delivered to the house but also on the temperatures outside and inside. The dependence on the temperature outside makes them impractical to use in areas where the temperature is much colder outside than room temperature.

In terms of energy costs, the heat pump is a very economical means for heating buildings ([\[link\]](#)). Contrast this method with turning electrical energy directly into heat with resistive heating elements. In this case, one unit of electrical energy furnishes at most only one unit of heat. Unfortunately, heat pumps have problems that do limit their usefulness. They are quite expensive to purchase compared to resistive heating elements, and, as the performance coefficient for a Carnot heat pump shows, they become less effective as the outside temperature decreases. In fact, below about $-10\text{ }^{\circ}\text{C}$, the heat they furnish is less than the energy used to operate them.



A photograph of a heat pump (large box) located outside a house. This heat pump is located in a warm climate area, like the southern United States, since it would be far too inefficient located in the northern half of the United States. (credit: modification of work by Peter Stevens)

Note:

Exercise:

Problem:

Check Your Understanding A Carnot engine operates between reservoirs at 400°C and 30°C . (a) What is the efficiency of the engine? (b) If the engine does 5.0 J of work per cycle, how much heat per cycle does it absorb from the high-temperature reservoir? (c) How much heat per cycle does it exhaust to the cold-temperature reservoir? (d) What temperatures at the cold reservoir would give the minimum and maximum efficiency?

Solution:

a. $e = 1 - T_c/T_h = 0.55$; b. $Q_h = eW = 9.1 \text{ J}$; c. $Q_c = Q_h - W = 4.1 \text{ J}$; d. -273°C and 400°C

Note:

Exercise:

Problem:

Check Your Understanding A Carnot refrigerator operates between two heat reservoirs whose temperatures are 0°C and 25°C . (a) What is the coefficient of performance of the refrigerator? (b) If 200 J of work are done on the working substance per cycle, how much heat per cycle is extracted from the cold reservoir? (c) How much heat per cycle is discarded to the hot reservoir?

Solution:

a. $K_R = T_c/(T_h - T_c) = 10.9$; b. $Q_c = K_RW = 2.18 \text{ kJ}$; c. $Q_h = Q_c + W = 2.38 \text{ kJ}$

Summary

- The Carnot cycle is the most efficient engine for a reversible cycle designed between two reservoirs.
- The Carnot principle is another way of stating the second law of thermodynamics.

Conceptual Questions

Exercise:

Problem:

To increase the efficiency of a Carnot engine, should the temperature of the hot reservoir be raised or lowered? What about the cold reservoir?

Solution:

In order to increase the efficiency, the temperature of the hot reservoir should be raised, and the cold reservoir should be lowered as much as possible. This can be seen in [\[link\]](#).

Exercise:

Problem: How could you design a Carnot engine with 100% efficiency?

Exercise:

Problem: What type of processes occur in a Carnot cycle?

Solution:

adiabatic and isothermal processes

Problems**Exercise:****Problem:**

The temperature of the cold and hot reservoirs between which a Carnot refrigerator operates are $-73\text{ }^{\circ}\text{C}$ and $270\text{ }^{\circ}\text{C}$, respectively. Which is its coefficient of performance?

Solution:

2.0

Exercise:**Problem:**

Suppose a Carnot refrigerator operates between T_c and T_h . Calculate the amount of work required to extract 1.0 J of heat from the cold reservoir if (a) $T_c = 7\text{ }^{\circ}\text{C}$, $T_h = 27\text{ }^{\circ}\text{C}$; (b) $T_c = -73\text{ }^{\circ}\text{C}$, $T_h = 27\text{ }^{\circ}\text{C}$; (c) $T_c = -173\text{ }^{\circ}\text{C}$, $T_h = 27\text{ }^{\circ}\text{C}$; and (d) $T_c = -273\text{ }^{\circ}\text{C}$, $T_h = 27\text{ }^{\circ}\text{C}$.

Exercise:

Problem:

A Carnot engine operates between reservoirs at 600 and 300 K. If the engine absorbs 100 J per cycle at the hot reservoir, what is its work output per cycle?

Solution:

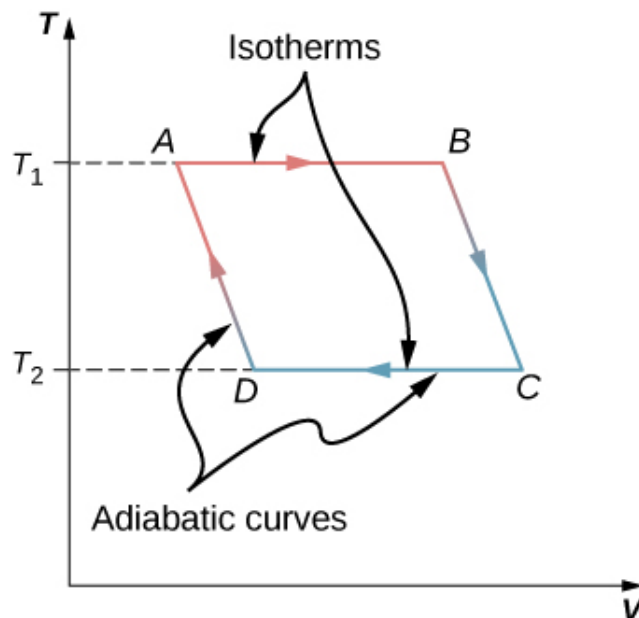
50 J

Exercise:**Problem:**

A 500-W motor operates a Carnot refrigerator between $-5\text{ }^{\circ}\text{C}$ and $30\text{ }^{\circ}\text{C}$. (a) What is the amount of heat per second extracted from the inside of the refrigerator? (b) How much heat is exhausted to the outside air per second?

Exercise:

Problem: Sketch a Carnot cycle on a temperature-volume diagram.

Solution:

Exercise:**Problem:**

A Carnot heat pump operates between 0°C and 20°C . How much heat is exhausted into the interior of a house for every 1.0 J of work done by the pump?

Exercise:**Problem:**

An engine operating between heat reservoirs at 20°C and 200°C extracts 1000 J per cycle from the hot reservoir. (a) What is the maximum possible work that engine can do per cycle? (b) For this maximum work, how much heat is exhausted to the cold reservoir per cycle?

Solution:

a. 900 J; b. 100 J

Exercise:**Problem:**

Suppose a Carnot engine can be operated between two reservoirs as either a heat engine or a refrigerator. How is the coefficient of performance of the refrigerator related to the efficiency of the heat engine?

Exercise:**Problem:**

A Carnot engine is used to measure the temperature of a heat reservoir. The engine operates between the heat reservoir and a reservoir consisting of water at its triple point. (a) If 400 J per cycle are removed from the heat reservoir while 200 J per cycle are deposited in the triple-point reservoir, what is the temperature of the heat reservoir? (b) If 400 J per cycle are removed from the triple-point reservoir while 200 J per cycle are deposited in the heat reservoir, what is the temperature of the heat reservoir?

Solution:

a. 546 K; b. 137 K

Exercise:**Problem:**

What is the minimum work required of a refrigerator if it is to extract 50 J per cycle from the inside of a freezer at $-10\text{ }^{\circ}\text{C}$ and exhaust heat to the air at $25\text{ }^{\circ}\text{C}$?

Glossary**Carnot cycle**

cycle that consists of two isotherms at the temperatures of two reservoirs and two adiabatic processes connecting the isotherms

Carnot engine

Carnot heat engine, refrigerator, or heat pump that operates on a Carnot cycle

Carnot principle

principle governing the efficiency or performance of a heat device operating on a Carnot cycle: any reversible heat device working between two reservoirs must have the same efficiency or performance coefficient, greater than that of an irreversible heat device operating between the same two reservoirs

Entropy

By the end of this section you will be able to:

- Describe the meaning of entropy
- Calculate the change of entropy for some simple processes

The second law of thermodynamics is best expressed in terms of a *change* in the thermodynamic variable known as **entropy**, which is represented by the symbol S . Entropy, like internal energy, is a state function. This means that when a system makes a transition from one state into another, the change in entropy ΔS is independent of path and depends only on the thermodynamic variables of the two states.

We first consider ΔS for a system undergoing a reversible process at a constant temperature. In this case, the change in entropy of the system is given by

Note:

Equation:

$$\Delta S = \frac{Q}{T},$$

where Q is the heat exchanged by the system kept at a temperature T (in kelvin). If the system absorbs heat—that is, with $Q > 0$ —the entropy of the system increases. As an example, suppose a gas is kept at a constant temperature of 300 K while it absorbs 10 J of heat in a reversible process. Then from [\[link\]](#), the entropy change of the gas is

Equation:

$$\Delta S = \frac{10 \text{ J}}{300 \text{ K}} = 0.033 \text{ J/K}.$$

Similarly, if the gas loses 5.0 J of heat; that is, $Q = -5.0 \text{ J}$, at temperature $T = 200 \text{ K}$, we have the entropy change of the system given by

Equation:

$$\Delta S = \frac{-5.0 \text{ J}}{200 \text{ K}} = -0.025 \text{ J/K}.$$

Example:

Entropy Change of Melting Ice

Heat is slowly added to a 50-g chunk of ice at 0°C until it completely melts into water at the same temperature. What is the entropy change of the ice?

Strategy

Because the process is slow, we can approximate it as a reversible process. The temperature is a constant, and we can therefore use [\[link\]](#) in the calculation.

Solution

The ice is melted by the addition of heat:

Equation:

$$Q = mL_f = 50 \text{ g} \times 335 \text{ J/g} = 16.8 \text{ kJ}.$$

In this reversible process, the temperature of the ice-water mixture is fixed at 0°C or 273 K . Now from $\Delta S = Q/T$, the entropy change of the ice is

Equation:

$$\Delta S = \frac{16.8 \text{ kJ}}{273 \text{ K}} = 61.5 \text{ J/K}$$

when it melts to water at 0°C .

Significance

During a phase change, the temperature is constant, allowing us to use [\[link\]](#) to solve this problem. The same equation could also be used if we changed from a liquid to a gas phase, since the temperature does not change during that process either.

The change in entropy of a system for an arbitrary, reversible transition for which the temperature is not necessarily constant is defined by modifying $\Delta S = Q/T$. Imagine a system making a transition from state A to B in small, discrete steps. The temperatures associated with these states are T_A and T_B , respectively. During each step of the transition, the system exchanges heat ΔQ_i reversibly at a temperature T_i . This can be accomplished experimentally by placing the system in thermal contact with a large number of heat reservoirs of varying temperatures T_i , as illustrated in [\[link\]](#). The change in entropy for each step is $\Delta S_i = Q_i/T_i$. The net change in entropy of the system for the transition is

Equation:

$$\Delta S = S_B - S_A = \sum_i \Delta S_i = \sum_i \frac{\Delta Q_i}{T_i}.$$

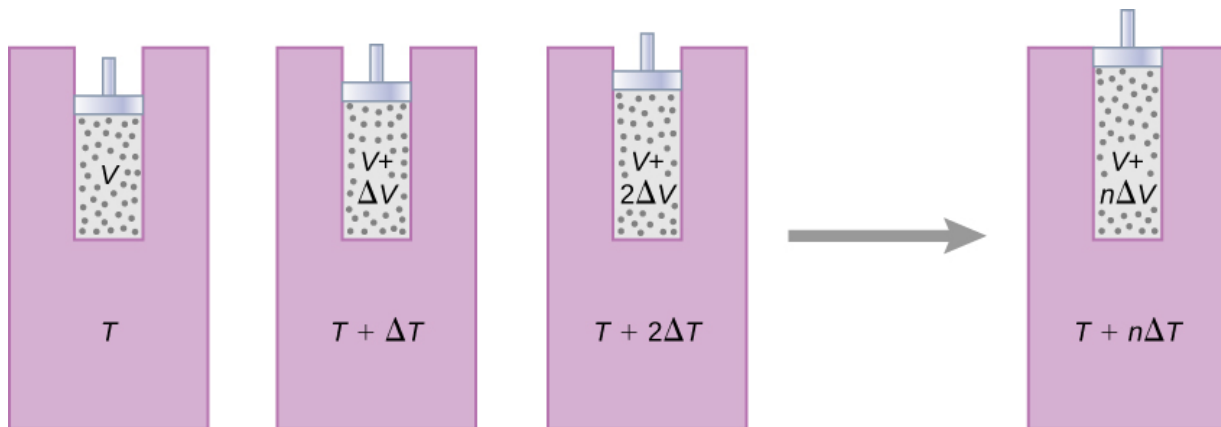
We now take the limit as $\Delta Q_i \rightarrow 0$, and the number of steps approaches infinity. Then, replacing the summation by an integral, we obtain

Note:

Equation:

$$\Delta S = S_B - S_A = \int_A^B \frac{dQ}{T},$$

where the integral is taken between the initial state A and the final state B . This equation is valid only if the transition from A to B is reversible.



The gas expands at constant pressure as its temperature is increased in small steps through the use of a series of heat reservoirs.

As an example, let us determine the net entropy change of a reversible engine while it undergoes a single Carnot cycle. In the adiabatic steps 2 and 4 of the cycle shown in [\[link\]](#), no heat exchange takes place, so

$\Delta S_2 = \Delta S_4 = \int dQ/T = 0$. In step 1, the engine absorbs heat Q_h at a temperature T_h , so its entropy change is $\Delta S_1 = Q_h/T_h$. Similarly, in step 3, $\Delta S_3 = -Q_c/T_c$. The net entropy change of the engine in one cycle of operation is then

Equation:

$$\Delta S_E = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = \frac{Q_h}{T_h} - \frac{Q_c}{T_c}.$$

However, we know that for a Carnot engine,

Equation:

$$\frac{Q_h}{T_h} = \frac{Q_c}{T_c},$$

so

Equation:

$$\Delta S_E = 0.$$

There is no net change in the entropy of the Carnot engine over a complete cycle. Although this result was obtained for a particular case, its validity can be shown to be far more general: There is no net change in the entropy of a system undergoing any complete reversible cyclic process.

Mathematically, we write this statement as

Note:**Equation:**

$$\oint dS = \oint \frac{dQ}{T} = 0$$

where \oint represents the integral over a *closed reversible path*.

We can use [\[link\]](#) to show that the entropy change of a system undergoing a reversible process between two given states is path independent. An arbitrary, closed path for a reversible cycle that passes through the states A and B is shown in [\[link\]](#). From [\[link\]](#), $\oint dS = 0$ for this closed path. We may split this integral into two segments, one along I, which leads from A to B , the other along II, which leads from B to A . Then

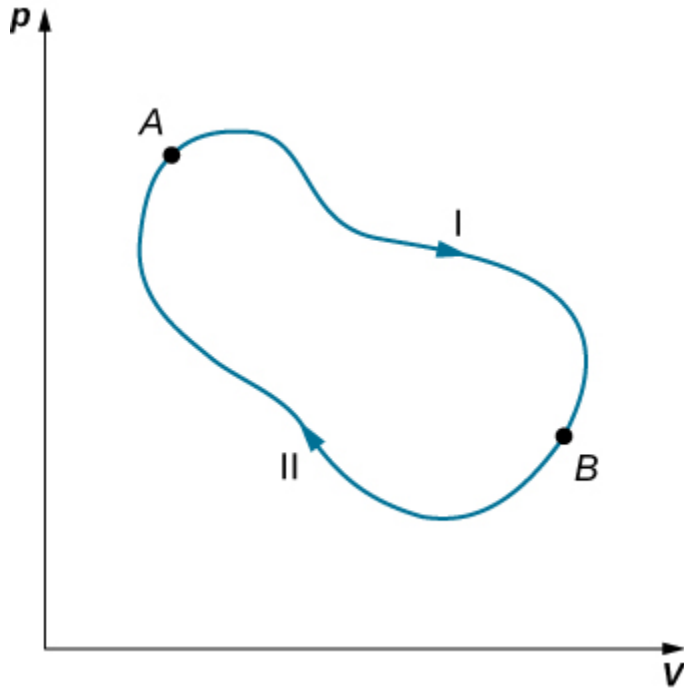
Equation:

$$\left[\int_A^B dS \right]_{\text{I}} + \left[\int_B^A dS \right]_{\text{II}} = 0.$$

Since the process is reversible,

Equation:

$$\left[\int_A^B dS \right]_{\text{I}} = \left[\int_A^B dS \right]_{\text{II}}.$$



The closed loop passing through states *A* and *B* represents a reversible cycle.

Hence, the entropy change in going from *A* to *B* is the same for paths I and II. Since paths I and II are arbitrary, reversible paths, the entropy change in a transition between two equilibrium states is the same for all the reversible processes joining these states. Entropy, like internal energy, is therefore a state function.

What happens if the process is irreversible? When the process is irreversible, we expect the entropy of a closed system, or the system and its

environment (the universe), to increase. Therefore we can rewrite this expression as

Note:

Equation:

$$\Delta S \geq 0,$$

where S is the total entropy of the closed system or the entire universe, and the equal sign is for a reversible process. The fact is the **entropy statement of the second law of thermodynamics**:

Note:

Second Law of Thermodynamics (Entropy statement)

The entropy of a closed system and the entire universe never decreases.

We can show that this statement is consistent with the Kelvin statement, the Clausius statement, and the Carnot principle.

Example:

Entropy Change of a System during an Isobaric Process

Determine the entropy change of an object of mass m and specific heat c that is cooled rapidly (and irreversibly) at constant pressure from T_h to T_c .

Strategy

The process is clearly stated as an irreversible process; therefore, we cannot simply calculate the entropy change from the actual process. However, because entropy of a system is a function of state, we can imagine a reversible process that starts from the same initial state and ends

at the given final state. Then, the entropy change of the system is given by [\[link\]](#), $\Delta S = \int_A^B dQ/T$.

Solution

To replace this rapid cooling with a process that proceeds reversibly, we imagine that the hot object is put into thermal contact with successively cooler heat reservoirs whose temperatures range from T_h to T_c .

Throughout the substitute transition, the object loses infinitesimal amounts of heat dQ , so we have

Equation:

$$\Delta S = \int_{T_h}^{T_c} \frac{dQ}{T}.$$

From the definition of heat capacity, an infinitesimal exchange dQ for the object is related to its temperature change dT by

Equation:

$$dQ = mc dT.$$

Substituting this dQ into the expression for ΔS , we obtain the entropy change of the object as it is cooled at constant pressure from T_h to T_c :

Equation:

$$\Delta S = \int_{T_h}^{T_c} \frac{mc dT}{T} = mc \ln \frac{T_c}{T_h}.$$

Note that $\Delta S < 0$ here because $T_c < T_h$. In other words, the object has lost some entropy. But if we count whatever is used to remove the heat from the object, we would still end up with $\Delta S_{\text{universe}} > 0$ because the process is irreversible.

Significance

If the temperature changes during the heat flow, you must keep it inside the integral to solve for the change in entropy. If, however, the temperature is constant, you can simply calculate the entropy change as the heat flow divided by the temperature.

Example:**Stirling Engine**

The steps of a reversible Stirling engine are as follows. For this problem, we will use 0.0010 mol of a monatomic gas that starts at a temperature of 133 °C and a volume of 0.10 m³, which will be called point A. Then it goes through the following steps:

1. Step *AB*: isothermal expansion at 133 °C from 0.10 m³ to 0.20 m³
2. Step *BC*: isochoric cooling to 33 °C
3. Step *CD*: isothermal compression at 33 °C from 0.20 m³ to 0.10 m³
4. Step *DA*: isochoric heating back to 133 °C and 0.10 m³

- (a) Draw the pV diagram for the Stirling engine with proper labels.
(b) Fill in the following table.

Step	W (J)	Q (J)	ΔS (J/K)
Step <i>AB</i>			
Step <i>BC</i>			
Step <i>CD</i>			
Step <i>DA</i>			
Complete cycle			

- (c) How does the efficiency of the Stirling engine compare to the Carnot engine working within the same two heat reservoirs?

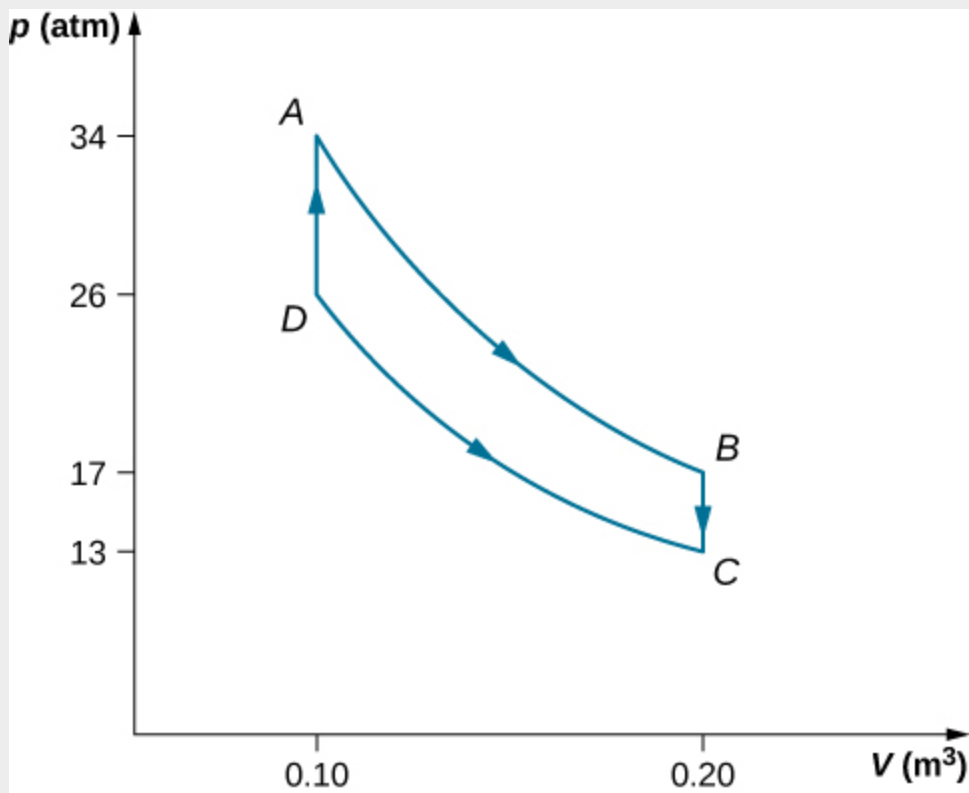
Strategy

Using the ideal gas law, calculate the pressure at each point so that they can be labeled on the pV diagram. Isothermal work is calculated using

$W = nRT \ln \left(\frac{V_2}{V_1} \right)$, and an isochoric process has no work done. The heat flow is calculated from the first law of thermodynamics, $Q = \Delta E_{\text{int}} - W$ where $\Delta E_{\text{int}} = \frac{3}{2}nR\Delta T$ for monatomic gasses. Isothermal steps have a change in entropy of Q/T , whereas isochoric steps have $\Delta S = \frac{3}{2}nR \ln \left(\frac{T_2}{T_1} \right)$. The efficiency of a heat engine is calculated by using $e_{\text{Stir}} = W/Q_{\text{h}}$.

Solution

a. The graph is shown below.



b. The completed table is shown below.

Step	W (J)	Q (J)	ΔS (J/K)
Step <i>AB</i> Isotherm	2.3	2.3	0.0057
Step <i>BC</i> Isochoric	0	−1.2	0.0035
Step <i>CD</i> Isotherm	−1.8	−1.8	−0.0059
Step <i>DA</i> Isochoric	0	1.2	−0.0035
Complete cycle	0.5	0.5	~ 0

c. The efficiency of the Stirling heat engine is

Equation:

$$e_{\text{Stir}} = W/Q_h = (Q_{AB} + Q_{CD})/(Q_{AB} + Q_{DA}) = 0.5/4.5 = 0.11.$$

If this were a Carnot engine operating between the same heat reservoirs, its efficiency would be

Equation:

$$e_{\text{Car}} = 1 - \left(\frac{T_c}{T_h} \right) = 0.25.$$

Therefore, the Carnot engine would have a greater efficiency than the Stirling engine.

Significance

In the early days of steam engines, accidents would occur due to the high pressure of the steam in the boiler. Robert Stirling developed an engine in 1816 that did not use steam and therefore was safer. The Stirling engine was commonly used in the nineteenth century, but developments in steam and internal combustion engines have made it difficult to broaden the use of the Stirling engine.

The Stirling engine uses compressed air as the working substance, which passes back and forth between two chambers with a porous plug, called the

regenerator, which is made of material that does not conduct heat as well. In two of the steps, pistons in the two chambers move in phase.

Summary

- The change in entropy for a reversible process at constant temperature is equal to the heat divided by the temperature. The entropy change of a system under a reversible process is given by $\Delta S = \int_A^B dQ/T$.
- A system's change in entropy between two states is independent of the reversible thermodynamic path taken by the system when it makes a transition between the states.

Conceptual Questions

Exercise:

Problem:

Does the entropy increase for a Carnot engine for each cycle?

Exercise:

Problem:

Is it possible for a system to have an entropy change if it neither absorbs nor emits heat during a reversible transition? What happens if the process is irreversible?

Solution:

Entropy will not change if it is a reversible transition but will change if the process is irreversible.

Problems

Exercise:

Problem:

Two hundred joules of heat are removed from a heat reservoir at a temperature of 200 K. What is the entropy change of the reservoir?

Solution:

-1 J/K

Exercise:

Problem:

In an isothermal reversible expansion at 27°C , an ideal gas does 20 J of work. What is the entropy change of the gas?

Exercise:

Problem:

An ideal gas at 300 K is compressed isothermally to one-fifth its original volume. Determine the entropy change per mole of the gas.

Solution:

-13 J/(K mole)

Exercise:

Problem:

What is the entropy change of 10 g of steam at 100°C when it condenses to water at the same temperature?

Exercise:

Problem:

A metal rod is used to conduct heat between two reservoirs at temperatures T_h and T_c , respectively. When an amount of heat Q flows through the rod from the hot to the cold reservoir, what is the net entropy change of the rod, the hot reservoir, the cold reservoir, and the universe?

Solution:

$$-\frac{Q}{T_h}, \frac{Q}{T_c}, Q \left(\frac{1}{T_c} - \frac{1}{T_h} \right)$$

Exercise:**Problem:**

For the Carnot cycle of [\[link\]](#), what is the entropy change of the hot reservoir, the cold reservoir, and the universe?

Exercise:**Problem:**

A 5.0-kg piece of lead at a temperature of 600°C is placed in a lake whose temperature is 15°C . Determine the entropy change of (a) the lead piece, (b) the lake, and (c) the universe.

Solution:

a. -540 J/K ; b. 1600 J/K ; c. 1100 J/K

Exercise:**Problem:**

One mole of an ideal gas doubles its volume in a reversible isothermal expansion. (a) What is the change in entropy of the gas? (b) If 1500 J of heat are added in this process, what is the temperature of the gas?

Exercise:

Problem:

One mole of an ideal monatomic gas is confined to a rigid container. When heat is added reversibly to the gas, its temperature changes from T_1 to T_2 . (a) How much heat is added? (b) What is the change in entropy of the gas?

Solution:

a. $Q = nR\Delta T$; b. $S = nR \ln(T_2/T_1)$

Exercise:**Problem:**

(a) A 5.0-kg rock at a temperature of 20°C is dropped into a shallow lake also at 20°C from a height of $1.0 \times 10^3\text{ m}$. What is the resulting change in entropy of the universe? (b) If the temperature of the rock is 100°C when it is dropped, what is the change of entropy of the universe? Assume that air friction is negligible (not a good assumption) and that $c = 860\text{ J/kg} \cdot \text{K}$ is the specific heat of the rock.

Glossary**entropy**

state function of the system that changes when heat is transferred between the system and the environment

entropy statement of the second law of thermodynamics

entropy of a closed system or the entire universe never decreases

Entropy on a Microscopic Scale

By the end of this section you will be able to:

- Interpret the meaning of entropy at a microscopic scale
- Calculate a change in entropy for an irreversible process of a system and contrast with the change in entropy of the universe
- Explain the third law of thermodynamics

We have seen how entropy is related to heat exchange at a particular temperature. In this section, we consider entropy from a statistical viewpoint. Although the details of the argument are beyond the scope of this textbook, it turns out that entropy can be related to how disordered or randomized a system is—the more it is disordered, the higher is its entropy. For example, a new deck of cards is very ordered, as the cards are arranged numerically by suit. In shuffling this new deck, we randomize the arrangement of the cards and therefore increase its entropy ([\[link\]](#)). Thus, by picking one card off the top of the deck, there would be no indication of what the next selected card will be.



The entropy of a new deck of cards goes up after the dealer shuffles them. (credit: “Rommel SK”/YouTube)

The second law of thermodynamics requires that the entropy of the universe increase in any irreversible process. Thus, in terms of order, the second law may be stated as follows:

In any irreversible process, the universe becomes more disordered. For example, the irreversible free expansion of an ideal gas, shown in [\[link\]](#), results in a larger volume for the gas molecules to occupy. A larger volume means more possible arrangements for the same number of atoms, so disorder is also increased. As a result, the entropy of the gas has gone up. The gas in this case is a closed system, and the process is irreversible. Changes in phase also illustrate the connection between entropy and **disorder**.

Example:**Entropy Change of the Universe**

Suppose we place 50 g of ice at 0°C in contact with a heat reservoir at 20°C . Heat spontaneously flows from the reservoir to the ice, which melts and eventually reaches a temperature of 20°C . Find the change in entropy of (a) the ice and (b) the universe.

Strategy

Because the entropy of a system is a function of its state, we can imagine two reversible processes for the ice: (1) ice is melted at $0^\circ\text{C}(T_A)$; and (2) melted ice (water) is warmed up from 0°C to $20^\circ\text{C}(T_B)$ under constant pressure. Then, we add the change in entropy of the reservoir when we calculate the change in entropy of the universe.

Solution

- a. From [\[link\]](#), the increase in entropy of the ice is

Equation:

$$\begin{aligned}
\Delta S_{\text{ice}} &= \Delta S_1 + \Delta S_2 \\
&= \frac{mL_f}{T_A} + mc \int_A^B \frac{dT}{T} \\
&= \left(\frac{50 \times 335}{273} + 50 \times 4.19 \times \ln \frac{293}{273} \right) \text{ J/K} \\
&= 76.3 \text{ J/K}.
\end{aligned}$$

b. During this transition, the reservoir gives the ice an amount of heat equal to

Equation:

$$\begin{aligned}
Q &= mL_f + mc(T_B - T_A) \\
&= 50 \times (335 + 4.19 \times 20) \text{ J} \\
&= 2.10 \times 10^4 \text{ J}.
\end{aligned}$$

This leads to a change (decrease) in entropy of the reservoir:

Equation:

$$\Delta S_{\text{reservoir}} = \frac{-Q}{T_B} = -71.7 \text{ J/K}.$$

The increase in entropy of the universe is therefore

Equation:

$$\Delta S_{\text{universe}} = 76.3 \text{ J/K} - 71.7 \text{ J/K} = 4.6 \text{ J/K} > 0.$$

Significance

The entropy of the universe therefore is greater than zero since the ice gains more entropy than the reservoir loses. If we considered only the phase change of the ice into water and not the temperature increase, the entropy change of the ice and reservoir would be the same, resulting in the universe gaining no entropy.

This process also results in a more disordered universe. The ice changes from a solid with molecules located at specific sites to a liquid whose molecules are much freer to move. The molecular arrangement has therefore become more randomized. Although the change in average kinetic energy of the molecules of the heat reservoir is negligible, there is nevertheless a significant decrease in the entropy of the reservoir because it has many more molecules than the melted ice cube. However, the reservoir's decrease in entropy is still not as large as the increase in entropy of the ice. The increased disorder of the ice more than compensates for the increased order of the reservoir, and the entropy of the universe increases by 4.6 J/K.

You might suspect that the growth of different forms of life might be a net ordering process and therefore a violation of the second law. After all, a single cell gathers molecules and eventually becomes a highly structured organism, such as a human being. However, this ordering process is more than compensated for by the disordering of the rest of the universe. The net result is an increase in entropy and an increase in the disorder of the universe.

Note:**Exercise:****Problem:**

Check Your Understanding In [\[link\]](#), the spontaneous flow of heat from a hot object to a cold object results in a net increase in entropy of the universe. Discuss how this result can be related to an increase in disorder of the system.

Solution:

When heat flows from the reservoir to the ice, the internal (mainly kinetic) energy of the ice goes up, resulting in a higher average speed and thus an average greater position variance of the molecules in the ice. The reservoir does become more ordered, but due to its much

larger amount of molecules, it does not offset the change in entropy in the system.

The second law of thermodynamics makes clear that the entropy of the universe never decreases during any thermodynamic process. For any other thermodynamic system, when the process is reversible, the change of the entropy is given by $\Delta S = Q/T$. But what happens if the temperature goes to zero, $T \rightarrow 0$? It turns out this is not a question that can be answered by the second law.

A fundamental issue still remains: Is it possible to cool a system all the way down to zero kelvin? We understand that the system must be at its lowest energy state because lowering temperature reduces the kinetic energy of the constituents in the system. What happens to the entropy of a system at the absolute zero temperature? It turns out the absolute zero temperature is not reachable—at least, not through a finite number of cooling steps. This is a statement of the **third law of thermodynamics**, whose proof requires quantum mechanics that we do not present here. In actual experiments, physicists have continuously pushed that limit downward, with the lowest temperature achieved at about 1×10^{-10} K in a low-temperature lab at the Helsinki University of Technology in 2008.

Like the second law of thermodynamics, the third law of thermodynamics can be stated in different ways. One of the common statements of the third law of thermodynamics is: *The absolute zero temperature cannot be reached through any finite number of cooling steps.*

In other words, the temperature of any given physical system must be finite, that is, $T > 0$. This produces a very interesting question in physics: Do we know how a system would behave if it were at the absolute zero temperature?

The reason a system is unable to reach 0 K is fundamental and requires quantum mechanics to fully understand its origin. But we can certainly ask what happens to the entropy of a system when we try to cool it down to 0

K. Because the amount of heat that can be removed from the system becomes vanishingly small, we expect that the change in entropy of the system along an isotherm approaches zero, that is,

Note:

Equation:

$$\lim_{T \rightarrow 0} (\Delta S)_T = 0.$$

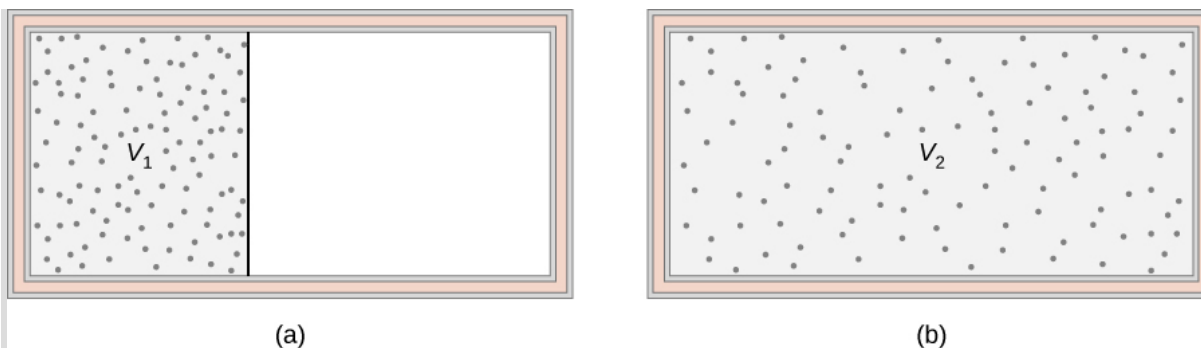
This can be viewed as another statement of the third law, with all the isotherms becoming **isentropic**, or into a reversible ideal adiabat. We can put this expression in words: *A system becomes perfectly ordered when its temperature approaches absolute zero and its entropy approaches its absolute minimum.*

The third law of thermodynamics puts another limit on what can be done when we look for energy resources. If there could be a reservoir at the absolute zero temperature, we could have engines with efficiency of 100%, which would, of course, violate the second law of thermodynamics.

Example:

Entropy Change of an Ideal Gas in Free Expansion

An ideal gas occupies a partitioned volume V_1 inside a box whose walls are thermally insulating, as shown in [\[link\]](#)(a). When the partition is removed, the gas expands and fills the entire volume V_2 of the box, as shown in part (b). What is the entropy change of the universe (the system plus its environment)?



The adiabatic free expansion of an ideal gas from volume V_1 to volume V_2 .

Strategy

The adiabatic free expansion of an ideal gas is an irreversible process. There is no change in the internal energy (and hence temperature) of the gas in such an expansion because no work or heat transfer has happened. Thus, a convenient reversible path connecting the same two equilibrium states is a slow, isothermal expansion from V_1 to V_2 . In this process, the gas could be expanding against a piston while in thermal contact with a heat reservoir, as in step 1 of the Carnot cycle.

Solution

Since the temperature is constant, the entropy change is given by $\Delta S = Q/T$, where

Equation:

$$Q = W = \int_{V_1}^{V_2} p dV$$

because $\Delta E_{\text{int}} = 0$. Now, with the help of the ideal gas law, we have

Equation:

$$Q = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \frac{V_2}{V_1},$$

so the change in entropy of the gas is

Equation:

$$\Delta S = \frac{Q}{T} = nR \ln \frac{V_2}{V_1}.$$

Because $V_2 > V_1$, ΔS is positive, and the entropy of the gas has gone up during the free expansion.

Significance

What about the environment? The walls of the container are thermally insulating, so no heat exchange takes place between the gas and its surroundings. The entropy of the environment is therefore constant during the expansion. The net entropy change of the universe is then simply the entropy change of the gas. Since this is positive, the entropy of the universe increases in the free expansion of the gas.

Example:

Entropy Change during Heat Transfer

Heat flows from a steel object of mass 4.00 kg whose temperature is 400 K to an identical object at 300 K. Assuming that the objects are thermally isolated from the environment, what is the net entropy change of the universe after thermal equilibrium has been reached?

Strategy

Since the objects are identical, their common temperature at equilibrium is 350 K. To calculate the entropy changes associated with their transitions, we substitute the irreversible process of the heat transfer by two isobaric, reversible processes, one for each of the two objects. The entropy change for each object is then given by $\Delta S = mc \ln(T_B/T_A)$.

Solution

Using $c = 450 \text{ J/kg} \cdot \text{K}$, the specific heat of steel, we have for the hotter object

Equation:

$$\begin{aligned} \Delta S_h &= \int_{T_1}^{T_2} \frac{mc dT}{T} = mc \ln \frac{T_2}{T_1} \\ &= (4.00 \text{ kg})(450 \text{ J/kg} \cdot \text{K}) \ln \frac{350 \text{ K}}{400 \text{ K}} = -240 \text{ J/K}. \end{aligned}$$

Similarly, the entropy change of the cooler object is

Equation:

$$\Delta S_c = (4.00 \text{ kg})(450 \text{ J/kg} \cdot \text{K}) \ln \frac{350 \text{ K}}{300 \text{ K}} = 277 \text{ J/K}.$$

The net entropy change of the two objects during the heat transfer is then

Equation:

$$\Delta S_h + \Delta S_c = 37 \text{ J/K}.$$

Significance

The objects are thermally isolated from the environment, so its entropy must remain constant. Thus, the entropy of the universe also increases by 37 J/K.

Note:**Exercise:****Problem:**

Check Your Understanding A quantity of heat Q is absorbed from a reservoir at a temperature T_h by a cooler reservoir at a temperature T_c . What is the entropy change of the hot reservoir, the cold reservoir, and the universe?

Solution:

$$-Q/T_h; Q/T_c; \text{ and } Q(T_h - T_c)/(T_h T_c)$$

Note:**Exercise:**

Problem:

Check Your Understanding A 50-g copper piece at a temperature of $20\text{ }^{\circ}\text{C}$ is placed into a large insulated vat of water at $100\text{ }^{\circ}\text{C}$. (a) What is the entropy change of the copper piece when it reaches thermal equilibrium with the water? (b) What is the entropy change of the water? (c) What is the entropy change of the universe?

Solution:

a. 4.71 J/K ; b. -4.18 J/K ; c. 0.53 J/K

Note:

View this [site](#) to learn about entropy and microstates. Start with a large barrier in the middle and 1000 molecules in only the left chamber. What is the total entropy of the system? Now remove the barrier and let the molecules travel from the left to the right hand side? What is the total entropy of the system now? Lastly, add heat and note what happens to the temperature. Did this increase entropy of the system?

Summary

- Entropy can be related to how disordered a system is—the more it is disordered, the higher is its entropy. In any irreversible process, the universe becomes more disordered.
- According to the third law of thermodynamics, absolute zero temperature is unreachable.

Key Equations

Result of energy conservation	$W = Q_h - Q_c$
Efficiency of a heat engine	$e = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h}$
Coefficient of performance of a refrigerator	$K_R = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c}$
Coefficient of performance of a heat pump	$K_P = \frac{Q_h}{W} = \frac{Q_h}{Q_h - Q_c}$
Resulting efficiency of a Carnot cycle	$e = 1 - \frac{T_c}{T_h}$
Performance coefficient of a reversible refrigerator	$K_R = \frac{T_c}{T_h - T_c}$
Performance coefficient of a reversible heat pump	$K_P = \frac{T_h}{T_h - T_c}$
Entropy of a system undergoing a reversible process at a constant temperature	$\Delta S = \frac{Q}{T}$
Change of entropy of a system under a reversible process	$\Delta S = S_B - S_A = \int_A^B dQ/T$
Entropy of a system undergoing any complete reversible cyclic process	$\oint dS = \oint \frac{dQ}{T} = 0$
Change of entropy of a closed system under an irreversible process	$\Delta S \geq 0$
Change in entropy of the system along an isotherm	$\lim_{T \rightarrow 0} (\Delta S)_T = 0$

Conceptual Questions

Exercise:

Problem:

Are the entropy changes of the *systems* in the following processes positive or negative? (a) *water vapor* that condenses on a cold surface; (b) gas in a container that leaks into the surrounding atmosphere; (c) an *ice cube* that melts in a glass of lukewarm water; (d) the *lukewarm water* of part (c); (e) a *real heat engine* performing a cycle; (f) *food* cooled in a refrigerator.

Exercise:

Problem:

Discuss the entropy changes in the systems of Question 21.10 in terms of disorder.

Solution:

Entropy is a function of disorder, so all the answers apply here as well.

Problems

Exercise:

Problem:

A copper rod of cross-sectional area 5.0 cm^2 and length 5.0 m conducts heat from a heat reservoir at 373 K to one at 273 K . What is the time rate of change of the universe's entropy for this process?

Solution:

$$3.78 \times 10^{-3} \text{ W/K}$$

Exercise:**Problem:**

Fifty grams of water at $20\text{ }^{\circ}\text{C}$ is heated until it becomes vapor at $100\text{ }^{\circ}\text{C}$. Calculate the change in entropy of the water in this process.

Exercise:**Problem:**

Fifty grams of water at $0\text{ }^{\circ}\text{C}$ are changed into vapor at $100\text{ }^{\circ}\text{C}$. What is the change in entropy of the water in this process?

Solution:

430 J/K

Exercise:**Problem:**

In an isochoric process, heat is added to 10 mol of monoatomic ideal gas whose temperature increases from 273 to 373 K. What is the entropy change of the gas?

Exercise:**Problem:**

Two hundred grams of water at $0\text{ }^{\circ}\text{C}$ is brought into contact with a heat reservoir at $80\text{ }^{\circ}\text{C}$. After thermal equilibrium is reached, what is the temperature of the water? Of the reservoir? How much heat has been transferred in the process? What is the entropy change of the water? Of the reservoir? What is the entropy change of the universe?

Solution:

$80\text{ }^{\circ}\text{C}$, $80\text{ }^{\circ}\text{C}$, $6.70 \times 10^4\text{ J}$, 215 J/K, -190 J/K , 25 J/K

Exercise:

Problem:

Suppose that the temperature of the water in the previous problem is raised by first bringing it to thermal equilibrium with a reservoir at a temperature of 40 °C and then with a reservoir at 80 °C. Calculate the entropy changes of (a) each reservoir, (b) of the water, and (c) of the universe.

Exercise:**Problem:**

Two hundred grams of water at 0 °C is brought into contact into thermal equilibrium successively with reservoirs at 20 °C, 40 °C, 60 °C, and 80 °C. (a) What is the entropy change of the water? (b) Of the reservoir? (c) What is the entropy change of the universe?

Solution:

$$\Delta S_{\text{H}_2\text{O}} = 215 \text{ J/K}, \Delta S_{\text{R}} = -208 \text{ J/K}, \Delta S_{\text{U}} = 7 \text{ J/K}$$

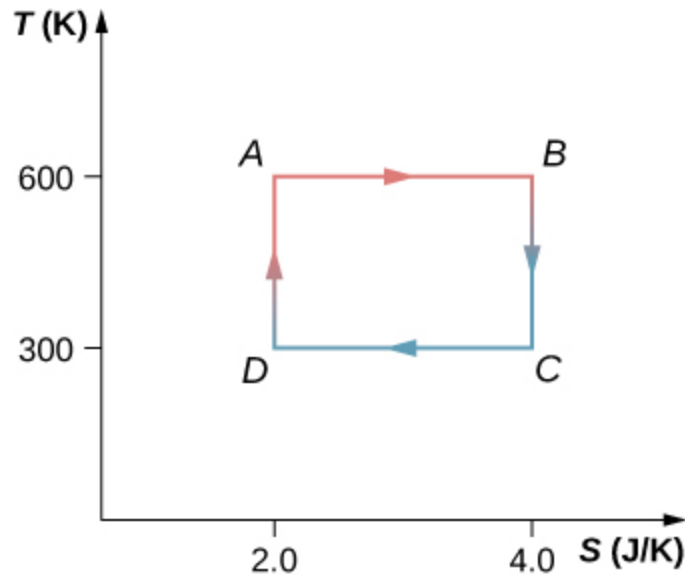
Exercise:**Problem:**

(a) Ten grams of H₂O starts as ice at 0 °C. The ice absorbs heat from the air (just above 0 °C) until all of it melts. Calculate the entropy change of the H₂O, of the air, and of the universe. (b) Suppose that the air in part (a) is at 20 °C rather than 0 °C and that the ice absorbs heat until it becomes water at 20 °C. Calculate the entropy change of the H₂O, of the air, and of the universe. (c) Is either of these processes reversible?

Exercise:

Problem:

The Carnot cycle is represented by the temperature-entropy diagram shown below. (a) How much heat is absorbed per cycle at the high-temperature reservoir? (b) How much heat is exhausted per cycle at the low-temperature reservoir? (c) How much work is done per cycle by the engine? (d) What is the efficiency of the engine?



Solution:

a. 1200 J; b. 600 J; c. 600 J; d. 0.50

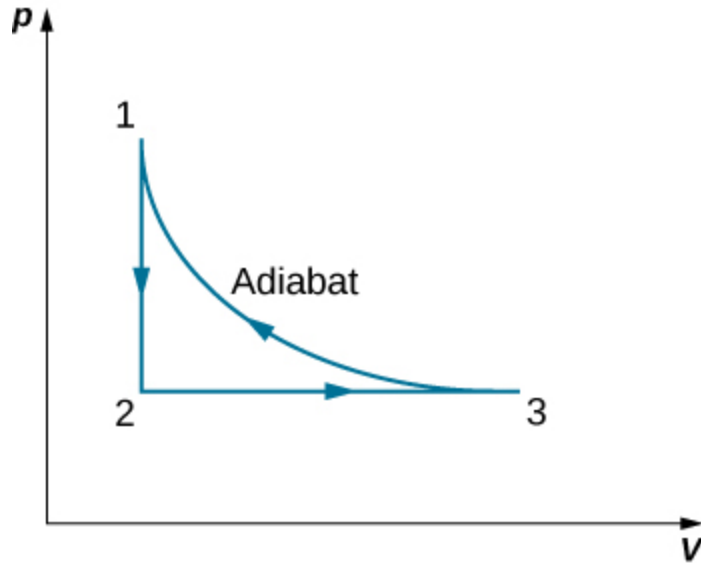
Exercise:**Problem:**

A Carnot engine operating between heat reservoirs at 500 and 300 K absorbs 1500 J per cycle at the high-temperature reservoir. (a) Represent the engine's cycle on a temperature-entropy diagram. (b) How much work per cycle is done by the engine?

Exercise:

Problem:

A monoatomic ideal gas (n moles) goes through a cyclic process shown below. Find the change in entropy of the gas in each step and the total entropy change over the entire cycle.



Solution:

$$\Delta S = nC_V \ln \left(\frac{T_2}{T_1} \right) + nC_p \ln \left(\frac{T_3}{T_2} \right)$$

Exercise:**Problem:**

A Carnot engine has an efficiency of 0.60. When the temperature of its cold reservoir changes, the efficiency drops to 0.55. If initially $T_c = 27^\circ \text{C}$, determine (a) the constant value of T_h and (b) the final value of T_c .

Exercise:

Problem:

A Carnot engine performs 100 J of work while discharging 200 J of heat each cycle. After the temperature of the hot reservoir only is adjusted, it is found that the engine now does 130 J of work while discarding the same quantity of heat. (a) What are the initial and final efficiencies of the engine? (b) What is the fractional change in the temperature of the hot reservoir?

Solution:

a. 0.33, 0.39; b. 0.91

Exercise:**Problem:**

A Carnot refrigerator exhausts heat to the air, which is at a temperature of 25 °C. How much power is used by the refrigerator if it freezes 1.5 g of water per second? Assume the water is at 0 °C.

Additional Problems**Exercise:****Problem:**

A 300-W heat pump operates between the ground, whose temperature is 0 °C, and the interior of a house at 22 °C. What is the maximum amount of heat per hour that the heat pump can supply to the house?

Solution:

$1.45 \times 10^7 \text{ J}$

Exercise:

Problem:

An engineer must design a refrigerator that does 300 J of work per cycle to extract 2100 J of heat per cycle from a freezer whose temperature is -10°C . What is the maximum air temperature for which this condition can be met? Is this a reasonable condition to impose on the design?

Exercise:**Problem:**

A Carnot engine employs 1.5 mol of nitrogen gas as a working substance, which is considered as an ideal diatomic gas with $\gamma = 7.5$ at the working temperatures of the engine. The Carnot cycle goes in the cycle $ABCD$ with AB being an isothermal expansion. The volume at points A and C of the cycle are $5.0 \times 10^{-3} \text{ m}^3$ and 0.15 L, respectively. The engine operates between two thermal baths of temperature 500 K and 300 K. (a) Find the values of volume at B and D . (b) How much heat is absorbed by the gas in the AB isothermal expansion? (c) How much work is done by the gas in the AB isothermal expansion? (d) How much heat is given up by the gas in the CD isothermal expansion? (e) How much work is done by the gas in the CD isothermal compression? (f) How much work is done by the gas in the BC adiabatic expansion? (g) How much work is done by the gas in the DA adiabatic compression? (h) Find the value of efficiency of the engine based on the net work and heat input. Compare this value to the efficiency of a Carnot engine based on the temperatures of the two baths.

Solution:

a. $V_B = 0.042 \text{ m}^3$, $V_D = 0.018 \text{ m}^3$; b. 13,000 J; c. 13,000 J; d. $-8,000 \text{ J}$; e. $-8,000 \text{ J}$; f. 6200 J; g. -6200 J ; h. 39%; with temperatures efficiency is 40%, which is off likely by rounding errors.

Exercise:

Problem:

A 5.0-kg wood block starts with an initial speed of 8.0 m/s and slides across the floor until friction stops it. Estimate the resulting change in entropy of the universe. Assume that everything stays at a room temperature of 20 °C.

Exercise:**Problem:**

A system consisting of 20.0 mol of a monoatomic ideal gas is cooled at constant pressure from a volume of 50.0 L to 10.0 L. The initial temperature was 300 K. What is the change in entropy of the gas?

Solution:

−670 J/K

Exercise:**Problem:**

A glass beaker of mass 400 g contains 500 g of water at 27 °C. The beaker is heated reversibly so that the temperature of the beaker and water rise gradually to 57 °C. Find the change in entropy of the beaker and water together.

Exercise:**Problem:**

A Carnot engine operates between 550 °C and 20 °C baths and produces 300 kJ of energy in each cycle. Find the change in entropy of the (a) hot bath and (b) cold bath, in each Carnot cycle?

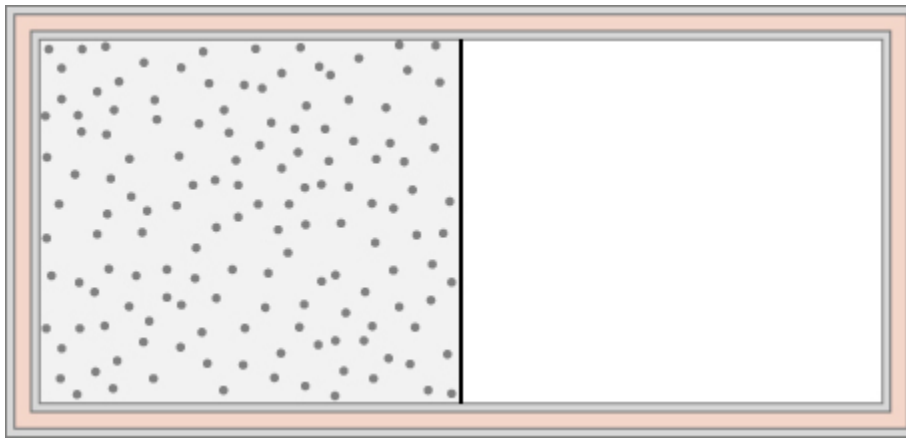
Solution:

a. −570 J/K; b. 570 J/K

Exercise:

Problem:

An ideal gas at temperature T is stored in the left half of an insulating container of volume V using a partition of negligible volume (see below). What is the entropy change per mole of the gas in each of the following cases? (a) The partition is suddenly removed and the gas quickly fills the entire container. (b) A tiny hole is punctured in the partition and after a long period, the gas reaches an equilibrium state such that there is no net flow through the hole. (c) The partition is moved very slowly and adiabatically all the way to the right wall so that the gas finally fills the entire container.

**Exercise:****Problem:**

A 0.50-kg piece of aluminum at 250°C is dropped into 1.0 kg of water at 20°C . After equilibrium is reached, what is the net entropy change of the system?

Solution:

82 J/K

Exercise:

Problem:

Suppose 20 g of ice at 0°C is added to 300 g of water at 60°C . What is the total change in entropy of the mixture after it reaches thermal equilibrium?

Exercise:**Problem:**

A heat engine operates between two temperatures such that the working substance of the engine absorbs 5000 J of heat from the high-temperature bath and discharges 3000 J to the low-temperature bath. The rest of the energy is converted into mechanical energy of the turbine. Find (a) the amount of work produced by the engine and (b) the efficiency of the engine.

Solution:

a. 2000 J; b. 40%

Exercise:**Problem:**

A thermal engine produces 4 MJ of electrical energy while operating between two thermal baths of different temperatures. The working substance of the engine discharges 5 MJ of heat to the cold temperature bath. What is the efficiency of the engine?

Exercise:**Problem:**

A coal power plant consumes 100,000 kg of coal per hour and produces 500 MW of power. If the heat of combustion of coal is 30 MJ/kg, what is the efficiency of the power plant?

Solution:

60%

Exercise:**Problem:**

A Carnot engine operates in a Carnot cycle between a heat source at $550\text{ }^{\circ}\text{C}$ and a heat sink at $20\text{ }^{\circ}\text{C}$. Find the efficiency of the Carnot engine.

Exercise:**Problem:**

A Carnot engine working between two heat baths of temperatures 600 K and 273 K completes each cycle in 5 sec . In each cycle, the engine absorbs 10 kJ of heat. Find the power of the engine.

Solution:

64.4%

Exercise:**Problem:**

A Carnot cycle working between $100\text{ }^{\circ}\text{C}$ and $30\text{ }^{\circ}\text{C}$ is used to drive a refrigerator between $-10\text{ }^{\circ}\text{C}$ and $30\text{ }^{\circ}\text{C}$. How much energy must the Carnot engine produce per second so that the refrigerator is able to discard 10 J of energy per second?

Challenge Problems**Exercise:****Problem:**

(a) An infinitesimal amount of heat is added reversibly to a system. By combining the first and second laws, show that $dU = TdS - dW$. (b) When heat is added to an ideal gas, its temperature and volume change from T_1 and V_1 to T_2 and V_2 . Show that the entropy change of n moles of the gas is given by

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}.$$

Solution:

derive

Exercise:

Problem:

Using the result of the preceding problem, show that for an ideal gas undergoing an adiabatic process, $TV^{\gamma-1}$ is constant.

Exercise:

Problem:

With the help of the two preceding problems, show that ΔS between states 1 and 2 of n moles an ideal gas is given by

$$\Delta S = nC_p \ln \frac{T_2}{T_1} - nR \ln \frac{p_2}{p_1}.$$

Solution:

derive

Exercise:

Problem:

A cylinder contains 500 g of helium at 120 atm and 20 °C. The valve is leaky, and all the gas slowly escapes isothermally into the atmosphere. Use the results of the preceding problem to determine the resulting change in entropy of the universe.

Exercise:

Problem:

A diatomic ideal gas is brought from an initial equilibrium state at $p_1 = 0.50$ atm and $T_1 = 300$ K to a final stage with $p_2 = 0.20$ atm and $T_2 = 500$ K. Use the results of the previous problem to determine the entropy change per mole of the gas.

Solution:

18 J/K

Exercise:**Problem:**

The gasoline internal combustion engine operates in a cycle consisting of six parts. Four of these parts involve, among other things, friction, heat exchange through finite temperature differences, and accelerations of the piston; it is irreversible. Nevertheless, it is represented by the ideal reversible *Otto cycle*, which is illustrated below. The working substance of the cycle is assumed to be air. The six steps of the Otto cycle are as follows:

- i. Isobaric intake stroke (*OA*). A mixture of gasoline and air is drawn into the combustion chamber at atmospheric pressure p_0 as the piston expands, increasing the volume of the cylinder from zero to V_A .
- ii. Adiabatic compression stroke (*AB*). The temperature of the mixture rises as the piston compresses it adiabatically from a volume V_A to V_B .
- iii. Ignition at constant volume (*BC*). The mixture is ignited by a spark. The combustion happens so fast that there is essentially no motion of the piston. During this process, the added heat Q_1 causes the pressure to increase from p_B to p_C at the constant volume $V_B (= V_C)$.
- iv. Adiabatic expansion (*CD*). The heated mixture of gasoline and air expands against the piston, increasing the volume from V_C to V_D .

This is called the *power stroke*, as it is the part of the cycle that delivers most of the power to the crankshaft.

- v. Constant-volume exhaust (*DA*). When the exhaust valve opens, some of the combustion products escape. There is almost no movement of the piston during this part of the cycle, so the volume remains constant at $V_A (= V_D)$. Most of the available energy is lost here, as represented by the heat exhaust Q_2 .
- vi. Isobaric compression (*AO*). The exhaust valve remains open, and the compression from V_A to zero drives out the remaining combustion products.

(a) Using (i) $e = W/Q_1$; (ii) $W = Q_1 - Q_2$; and (iii) $Q_1 = nC_v(T_C - T_B)$, $Q_2 = nC_v(T_D - T_A)$, show that

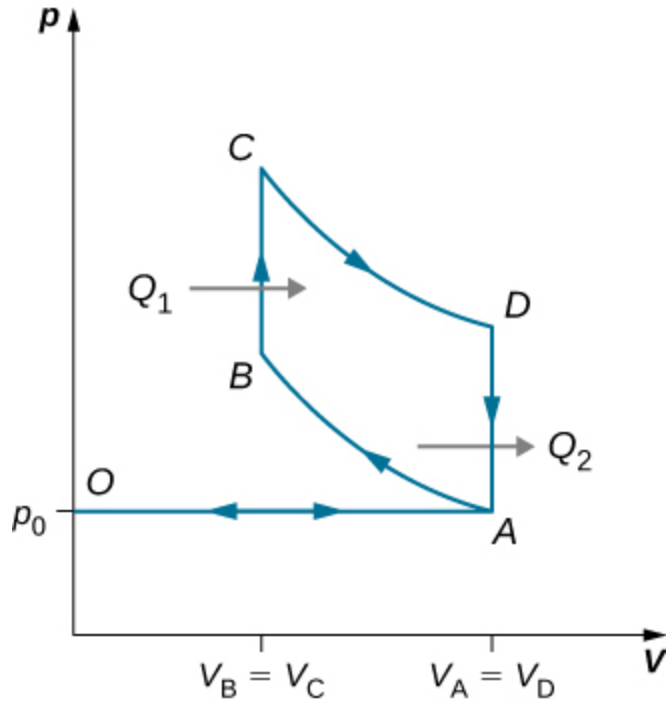
$$e = 1 - \frac{T_D - T_A}{T_C - T_B}.$$

(b) Use the fact that steps (ii) and (iv) are adiabatic to show that

$$e = 1 - \frac{1}{r^{\gamma-1}},$$

where $r = V_A/V_B$. The quantity r is called the *compression ratio* of the engine.

(c) In practice, r is kept less than around 7. For larger values, the gasoline-air mixture is compressed to temperatures so high that it explodes before the finely timed spark is delivered. This *preignition* causes engine knock and loss of power. Show that for $r = 6$ and $\gamma = 1.4$ (the value for air), $e = 0.51$, or an efficiency of 51%. Because of the many irreversible processes, an actual internal combustion engine has an efficiency much less than this ideal value. A typical efficiency for a tuned engine is about 25% to 30%.



Exercise:

Problem:

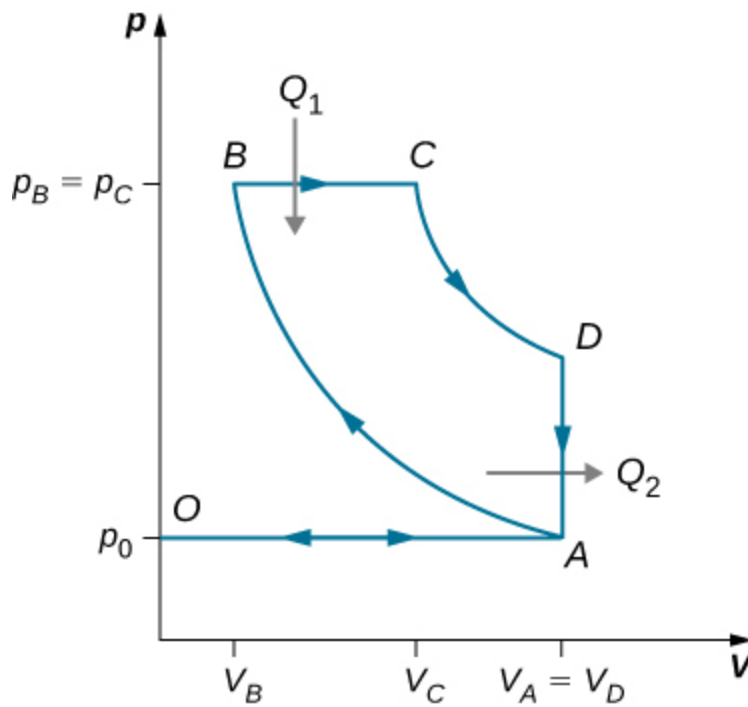
An ideal *diesel* cycle is shown below. This cycle consists of five strokes. In this case, only air is drawn into the chamber during the intake stroke OA . The air is then compressed adiabatically from state A to state B , raising its temperature high enough so that when fuel is added during the power stroke BC , it ignites. After ignition ends at C , there is a further adiabatic power stroke CD . Finally, there is an exhaust at constant volume as the pressure drops from p_D to p_A , followed by a further exhaust when the piston compresses the chamber volume to zero.

(a) Use $W = Q_1 - Q_2$, $Q_1 = nC_p(T_C - T_B)$, and $Q_2 = nC_v(T_D - T_A)$ to show that $e = \frac{W}{Q_1} = 1 - \frac{T_D - T_A}{\gamma(T_C - T_B)}$.

(b) Use the fact that $A \rightarrow B$ and $C \rightarrow D$ are adiabatic to show that

$$e = 1 - \frac{1}{\gamma} \frac{\left(\frac{V_C}{V_D}\right)^\gamma - \left(\frac{V_B}{V_A}\right)^\gamma}{\left(\frac{V_C}{V_D}\right) - \left(\frac{V_B}{V_A}\right)}.$$

(c) Since there is no preignition (remember, the chamber does not contain any fuel during the compression), the compression ratio can be larger than that for a gasoline engine. Typically, $V_A/V_B = 15$ and $V_D/V_C = 5$. For these values and $\gamma = 1.4$, show that $\epsilon = 0.56$, or an efficiency of 56%. Diesel engines actually operate at an efficiency of about 30% to 35% compared with 25% to 30% for gasoline engines.



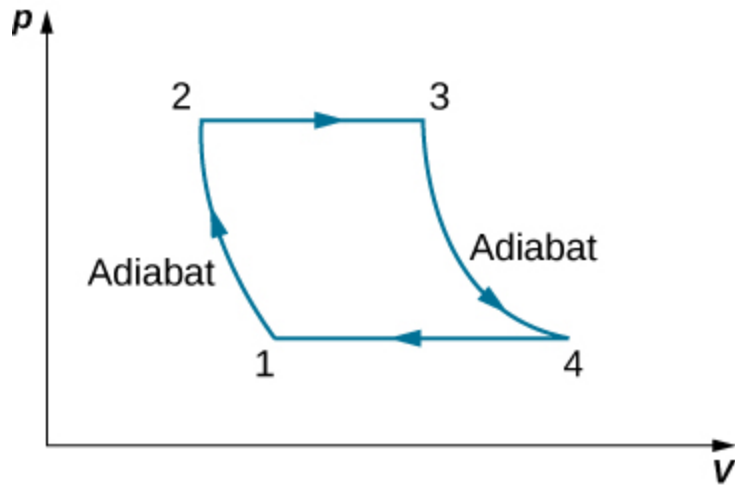
Solution:

proof

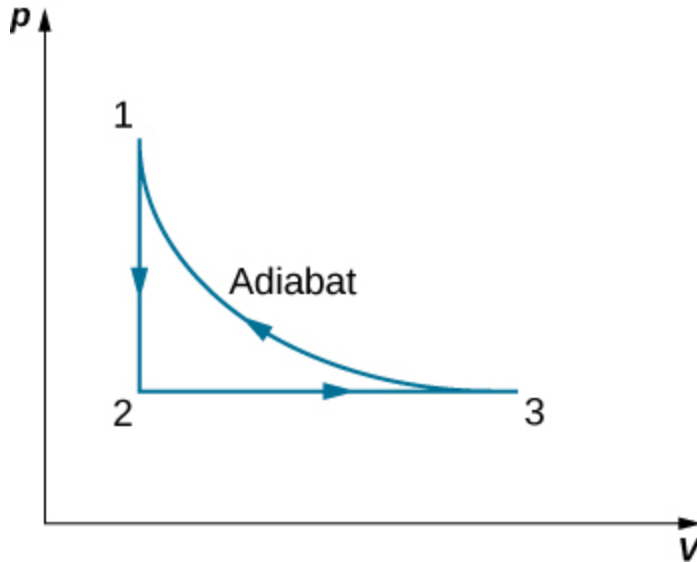
Exercise:

Problem:

Consider an ideal gas Joule cycle, also called the Brayton cycle, shown below. Find the formula for efficiency of the engine using this cycle in terms of P_1 , P_2 , and γ .

**Exercise:****Problem:**

Derive a formula for the coefficient of performance of a refrigerator using an ideal gas as a working substance operating in the cycle shown below in terms of the properties of the three states labeled 1, 2, and 3.



Solution:

$$K_R = \frac{3(p_1 - p_2)V_1}{5p_2V_3 - 3p_1V_1 - p_2V_1}$$

Exercise:

Problem:

Two moles of nitrogen gas, with $\gamma = 7/5$ for ideal diatomic gases, occupies a volume of 10^{-2}m^3 in an insulated cylinder at temperature 300 K. The gas is adiabatically and reversibly compressed to a volume of 5 L. The piston of the cylinder is locked in its place, and the insulation around the cylinder is removed. The heat-conducting cylinder is then placed in a 300-K bath. Heat from the compressed gas leaves the gas, and the temperature of the gas becomes 300 K again. The gas is then slowly expanded at the fixed temperature 300 K until the volume of the gas becomes 10^{-2}m^3 , thus making a complete cycle for the gas. For the entire cycle, calculate (a) the work done by the gas, (b) the heat into or out of the gas, (c) the change in the internal energy of the gas, and (d) the change in entropy of the gas.

Exercise:

Problem:

A Carnot refrigerator, working between $0\text{ }^{\circ}\text{C}$ and $30\text{ }^{\circ}\text{C}$ is used to cool a bucket of water containing 10^{-2} m^3 of water at $30\text{ }^{\circ}\text{C}$ to $5\text{ }^{\circ}\text{C}$ in 2 hours. Find the total amount of work needed.

Solution:

$$W = 110,000\text{ J}$$

Glossary

disorder

measure of order in a system; the greater the disorder is, the higher the entropy

isentropic

reversible adiabatic process where the process is frictionless and no heat is transferred

third law of thermodynamics

absolute zero temperature cannot be reached through any finite number of cooling steps

Units

Quantity	Common Symbol	Unit	Unit in Terms of Base SI Units
Acceleration		m/s ²	m/s ²
Amount of substance	<i>n</i>	mole	mol
Angle	,	radian (rad)	
Angular acceleration		rad/s ²	s ⁻²
Angular frequency		rad/s	s ⁻¹
Angular momentum		kg · m ² /s	kg · m ² /s
Angular velocity		rad/s	s ⁻¹
Area	<i>A</i>	m ²	m ²
Atomic number	<i>Z</i>		
Capacitance	<i>C</i>	farad (F)	A ² · s ⁴ /kg · m ²
Charge	<i>q</i> , <i>Q</i> , <i>e</i>	coulomb (C)	A · s
Charge density:			
Line		C/m	A · s/m
Surface		C/m ²	A · s/m ²
Volume		C/m ³	A · s/m ³

Quantity	Common Symbol	Unit	Unit in Terms of Base SI Units
Conductivity		$1/\Omega \cdot \text{m}$	$\text{A}^2 \cdot \text{s}^3/\text{kg} \cdot \text{m}^3$
Current	I	ampere	A
Current density		A/m^2	A/m^2
Density		kg/m^3	kg/m^3
Dielectric constant			
Electric dipole moment		$\text{C} \cdot \text{m}$	$\text{A} \cdot \text{s} \cdot \text{m}$
Electric field		N/C	$\text{kg} \cdot \text{m}/\text{A} \cdot \text{s}^3$
Electric flux	Φ	$\text{N} \cdot \text{m}^2/\text{C}$	$\text{kg} \cdot \text{m}^3/\text{A} \cdot \text{s}^3$
Electromotive force	ε	volt (V)	$\text{kg} \cdot \text{m}^2/\text{A} \cdot \text{s}^3$
Energy	E, U, K	joule (J)	$\text{kg} \cdot \text{m}^2/\text{s}^2$
Entropy	S	J/K	$\text{kg} \cdot \text{m}^2/\text{s}^2 \cdot \text{K}$
Force		newton (N)	$\text{kg} \cdot \text{m}/\text{s}^2$
Frequency	f	hertz (Hz)	s^{-1}
Heat	Q	joule (J)	$\text{kg} \cdot \text{m}^2/\text{s}^2$
Inductance	L	henry (H)	$\text{kg} \cdot \text{m}^2/\text{A}^2 \cdot \text{s}^2$
Length:	$\ell,$	meter	m
Displacement	Δ, Δ		
Distance	d, h		
Position	$, , ,$		

Quantity	Common Symbol	Unit	Unit in Terms of Base SI Units
Magnetic dipole moment		$\text{N} \cdot \text{J}/\text{T}$	$\text{A} \cdot \text{m}^2$
Magnetic field		tesla (T) = Wb/m^2	$\text{kg}/\text{A} \cdot \text{s}^2$
Magnetic flux	Φ_{m}	weber (Wb)	$\text{kg} \cdot \text{m}^2/\text{A} \cdot \text{s}^2$
Mass	m, M	kilogram	kg
Molar specific heat	C	$\text{J}/\text{mol} \cdot \text{K}$	$\text{kg} \cdot \text{m}^2/\text{s}^2 \cdot \text{mol} \cdot \text{K}$
Moment of inertia	I	$\text{kg} \cdot \text{m}^2$	$\text{kg} \cdot \text{m}^2$
Momentum		$\text{kg} \cdot \text{m}/\text{s}$	$\text{kg} \cdot \text{m}/\text{s}$
Period	T	s	s
Permeability of free space	μ_0	$\text{N}/\text{A}^2 = (\text{H}/\text{m})$	$\text{kg} \cdot \text{m}/\text{A}^2 \cdot \text{s}^2$
Permittivity of free space	ϵ_0	$\text{C}^2/\text{N} \cdot \text{m}^2 = (\text{F}/\text{m})$	$\text{A}^2 \cdot \text{s}^4/\text{kg} \cdot \text{m}^3$
Potential	V	volt (V) = (J/C)	$\text{kg} \cdot \text{m}^2/\text{A} \cdot \text{s}^3$
Power	P	watt (W) = (J/s)	$\text{kg} \cdot \text{m}^2/\text{s}^3$
Pressure	p	pascal (Pa) = N/m^2	$\text{kg}/\text{m} \cdot \text{s}^2$
Resistance	R	ohm (Ω) = (V/A)	$\text{kg} \cdot \text{m}^2/\text{A}^2 \cdot \text{s}^3$
Specific heat	c	$\text{J}/\text{kg} \cdot \text{K}$	$\text{m}^2/\text{s}^2 \cdot \text{K}$
Speed		m/s	m/s
Temperature	T	kelvin	K
Time	t	second	s

Quantity	Common Symbol	Unit	Unit in Terms of Base SI Units
Torque		$\text{N} \cdot \text{m}$	$\text{kg} \cdot \text{m}^2/\text{s}^2$
Velocity		m/s	m/s
Volume	V	m^3	m^3
Wavelength		m	m
Work	W	joule (J) = $(\text{N} \cdot \text{m})$	$\text{kg} \cdot \text{m}^2/\text{s}^2$

Units Used in Physics (Fundamental units in bold)

Conversion Factors

	m	cm	km
1 meter	1	10^2	10^{-3}
1 centimeter	10^{-2}	1	10^{-5}
1 kilometer	10^3	10^5	1
1 inch	2.540×10^{-2}	2.540	2.540×10^{-5}
1 foot	0.3048	30.48	3.048×10^{-4}
1 mile	1609	1.609×10^4	1.609
1 angstrom	10^{-10}		
1 fermi	10^{-15}		
1 light-year			9.460×10^{12}
	in.	ft	mi
1 meter	39.37	3.281	6.214×10^{-4}
1 centimeter	0.3937	3.281×10^{-2}	6.214×10^{-6}
1 kilometer	3.937×10^4	3.281×10^3	0.6214
1 inch	1	8.333×10^{-2}	1.578×10^{-5}
1 foot	12	1	1.894×10^{-4}
1 mile	6.336×10^4	5280	1

Length

Area

$$1 \text{ cm}^2 = 0.155 \text{ in.}^2$$

$$1 \text{ m}^2 = 10^4 \text{ cm}^2 = 10.76 \text{ ft}^2$$

$$1 \text{ in.}^2 = 6.452 \text{ cm}^2$$

$$1 \text{ ft}^2 = 144 \text{ in.}^2 = 0.0929 \text{ m}^2$$

Volume

$$1 \text{ liter} = 1000 \text{ cm}^3 = 10^{-3} \text{ m}^3 = 0.03531 \text{ ft}^3 = 61.02 \text{ in.}^3$$

$$1 \text{ ft}^3 = 0.02832 \text{ m}^3 = 28.32 \text{ liters} = 7.477 \text{ gallons}$$

$$1 \text{ gallon} = 3.788 \text{ liters}$$

	s	min	h	day	yr
1 second	1	1.667×10^{-2}	2.778×10^{-4}	1.157×10^{-5}	3.169×10^{-8}
1 minute	60	1	1.667×10^{-2}	6.944×10^{-4}	1.901×10^{-6}
1 hour	3600	60	1	4.167×10^{-2}	1.141×10^{-4}
1 day	8.640×10^4	1440	24	1	2.738×10^{-3}
1 year	3.156×10^7	5.259×10^5	8.766×10^3	365.25	1

Time

	m/s	cm/s	ft/s	mi/h
1 meter/second	1	10^2	3.281	2.237
1 centimeter/second	10^{-2}	1	3.281×10^{-2}	2.237×10^{-2}
1 foot/second	0.3048	30.48	1	0.6818
1 mile/hour	0.4470	44.70	1.467	1

Speed

Acceleration

$$1 \text{ m/s}^2 = 100 \text{ cm/s}^2 = 3.281 \text{ ft/s}^2$$

$$1 \text{ cm/s}^2 = 0.01 \text{ m/s}^2 = 0.03281 \text{ ft/s}^2$$

$$1 \text{ ft/s}^2 = 0.3048 \text{ m/s}^2 = 30.48 \text{ cm/s}^2$$

$$1 \text{ mi/h} \cdot \text{s} = 1.467 \text{ ft/s}^2$$

	kg	g	slug	u
1 kilogram	1	10^3	6.852×10^{-2}	6.024×10^{26}
1 gram	10^{-3}	1	6.852×10^{-5}	6.024×10^{23}
1 slug	14.59	1.459×10^4	1	8.789×10^{27}
1 atomic mass unit	1.661×10^{-27}	1.661×10^{-24}	1.138×10^{-28}	1
1 metric ton	1000			

Mass

	N	dyne	lb
1 newton	1	10^5	0.2248
1 dyne	10^{-5}	1	2.248×10^{-6}
1 pound	4.448	4.448×10^5	1

Force

	Pa	dyne/cm²	atm	cmHg	lb/in.²
1 pascal	1	10	9.869×10^{-6}	7.501×10^{-4}	1.450×10^{-4}
1 dyne/centimeter ²	10^{-1}	1	9.869×10^{-7}	7.501×10^{-5}	1.450×10^{-5}
1 atmosphere	1.013×10^5	1.013×10^6	1	76	14.70
1 centimeter mercury*	1.333×10^3	1.333×10^4	1.316×10^{-2}	1	0.1934
1 pound/inch ²	6.895×10^3	6.895×10^4	6.805×10^{-2}	5.171	1
1 bar	10^5				
1 torr				1 (mmHg)	
*Where the acceleration due to gravity is 9.80665 m/s^2 and the temperature is 0°C					

Pressure

	J	erg	ft.lb
1 joule	1	10^7	0.7376
1 erg	10^{-7}	1	7.376×10^{-8}
1 foot-pound	1.356	1.356×10^7	1
1 electron-volt	1.602×10^{-19}	1.602×10^{-12}	1.182×10^{-19}
1 calorie	4.186	4.186×10^7	3.088
1 British thermal unit	1.055×10^3	1.055×10^{10}	7.779×10^2
1 kilowatt-hour	3.600×10^6		
	eV	cal	Btu
1 joule	6.242×10^{18}	0.2389	9.481×10^{-4}
1 erg	6.242×10^{11}	2.389×10^{-8}	9.481×10^{-11}
1 foot-pound	8.464×10^{18}	0.3239	1.285×10^{-3}
1 electron-volt	1	3.827×10^{-20}	1.519×10^{-22}
1 calorie	2.613×10^{19}	1	3.968×10^{-3}
1 British thermal unit	6.585×10^{21}	2.520×10^2	1

Work, Energy, Heat

Power

$$1 \text{ W} = 1 \text{ J/s}$$

$$1 \text{ hp} = 746 \text{ W} = 550 \text{ ft} \cdot \text{lb/s}$$

$$1 \text{ Btu/h} = 0.293 \text{ W}$$

Angle

$$1 \text{ rad} = 57.30^\circ = 180^\circ/\pi$$

$$1^\circ = 0.01745 \text{ rad} = \pi/180 \text{ rad}$$

$$1 \text{ revolution} = 360^\circ = 2\pi \text{ rad}$$

$$1 \text{ rev/min (rpm)} = 0.1047 \text{ rad/s}$$

Fundamental Constants

Quantity	Symbol	Value
Atomic mass unit	u	$1.660\,538\,782\,(83) \times 10^{-27}\,\text{kg}$ $931.494\,028\,(23)\,\text{MeV}/c^2$
Avogadro's number	N_A	$6.022\,141\,79\,(30) \times 10^{23}\,\text{particles/mol}$
Bohr magneton	$\mu_B = \frac{e\hbar}{2m_e}$	$9.274\,009\,15\,(23) \times 10^{-24}\,\text{J/T}$
Bohr radius	$a_0 = \frac{\hbar^2}{m_e e^2 k_e}$	$5.291\,772\,085\,9\,(36) \times 10^{-11}\,\text{m}$
Boltzmann's constant	$k_B = \frac{R}{N_A}$	$1.380\,650\,4\,(24) \times 10^{-23}\,\text{J/K}$
Compton wavelength	$\lambda_C = \frac{h}{m_e c}$	$2.426\,310\,217\,5\,(33) \times 10^{-12}\,\text{m}$
Coulomb constant	$k_e = \frac{1}{4\pi\epsilon_0}$	$8.987\,551\,788\dots \times 10^9\,\text{N} \cdot \text{m}^2/\text{C}^2\,(\text{exact})$
Deuteron mass	m_d	$3.343\,583\,20\,(17) \times 10^{-27}\,\text{kg}$ $2.013\,553\,212\,724\,(78)\,\text{u}$ $1875.612\,859\,\text{MeV}/c^2$
Electron mass	m_e	$9.109\,382\,15\,(45) \times 10^{-31}\,\text{kg}$ $5.485\,799\,094\,3\,(23) \times 10^{-4}\,\text{u}$ $0.510\,998\,910\,(13)\,\text{MeV}/c^2$
Electron volt	eV	$1.602\,176\,487\,(40) \times 10^{-19}\,\text{J}$

Quantity	Symbol	Value
Elementary charge	e	$1.602\,176\,487\,(40) \times 10^{-19} \text{ C}$
Gas constant	R	$8.314\,472\,(15) \text{ J/mol} \cdot \text{K}$
Gravitational constant	G	$6.674\,28\,(67) \times 10^{-11} \text{ N} \cdot \text{m}^2/\text{kg}^2$
Neutron mass	m_n	$1.674\,927\,211\,(84) \times 10^{-27} \text{ kg}$ $1.008\,664\,915\,97\,(43) \text{ u}$ $939.565\,346\,(23) \text{ MeV}/c^2$
Nuclear magneton	$\mu_n = \frac{e\hbar}{2m_p}$	$5.050\,783\,24\,(13) \times 10^{-27} \text{ J/T}$
Permeability of free space	μ_0	$4\pi \times 10^{-7} \text{ T} \cdot \text{m/A (exact)}$
Permittivity of free space	$\epsilon_0 = \frac{1}{\mu_0 c^2}$	$8.854\,187\,817... \times 10^{-12} \text{ C}^2/\text{N} \cdot \text{m}^2 \text{ (exact)}$
Planck's constant	h $\hbar = \frac{h}{2\pi}$	$6.626\,068\,96\,(33) \times 10^{-34} \text{ J} \cdot \text{s}$ $1.054\,571\,628\,(53) \times 10^{-34} \text{ J} \cdot \text{s}$
Proton mass	m_p	$1.672\,621\,637\,(83) \times 10^{-27} \text{ kg}$ $1.007\,276\,466\,77\,(10) \text{ u}$ $938.272\,013\,(23) \text{ MeV}/c^2$
Rydberg constant	R_H	$1.097\,373\,156\,852\,7\,(73) \times 10^7 \text{ m}^{-1}$
Speed of light in vacuum	c	$2.997\,924\,58 \times 10^8 \text{ m/s (exact)}$

Fundamental Constants*Note:* These constants are the values recommended in 2006 by CODATA, based on a least-squares adjustment of data from different measurements. The numbers in parentheses for the values represent the uncertainties of the last two digits.

Useful combinations of constants for calculations:

$$hc = 12,400 \text{ eV} \cdot \text{\AA} = 1240 \text{ eV} \cdot \text{nm} = 1240 \text{ MeV} \cdot \text{fm}$$

$$\hbar c = 1973 \text{ eV} \cdot \text{\AA} = 197.3 \text{ eV} \cdot \text{nm} = 197.3 \text{ MeV} \cdot \text{fm}$$

$$k_e e^2 = 14.40 \text{ eV} \cdot \text{\AA} = 1.440 \text{ eV} \cdot \text{nm} = 1.440 \text{ MeV} \cdot \text{fm}$$

$$k_B T = 0.02585 \text{ eV at } T = 300 \text{ K}$$

Mathematical Formulas

Quadratic formula

If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Triangle of base b and height h	Area $= \frac{1}{2}bh$	
Circle of radius r	Circumference $= 2\pi r$	Area $= \pi r^2$
Sphere of radius r	Surface area $= 4\pi r^2$	Volume $= \frac{4}{3}\pi r^3$
Cylinder of radius r and height h	Area of curved surface $= 2\pi rh$	Volume $= \pi r^2 h$

Geometry

Trigonometry

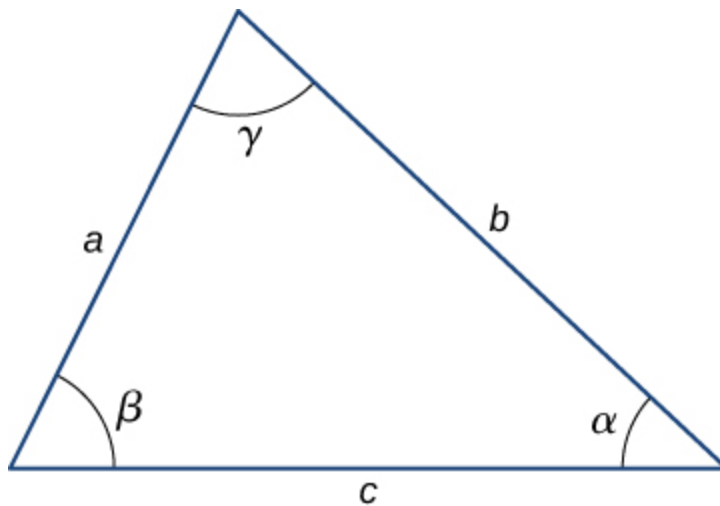
Trigonometric Identities

1. $\sin \theta = 1/\csc \theta$
2. $\cos \theta = 1/\sec \theta$
3. $\tan \theta = 1/\cot \theta$
4. $\sin (90^\circ - \theta) = \cos \theta$
5. $\cos (90^\circ - \theta) = \sin \theta$
6. $\tan (90^\circ - \theta) = \cot \theta$
7. $\sin^2 \theta + \cos^2 \theta = 1$
8. $\sec^2 \theta - \tan^2 \theta = 1$

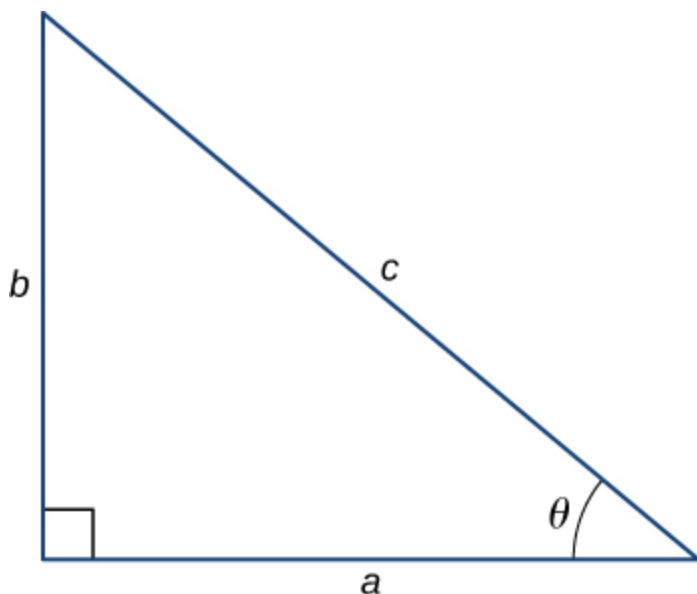
9. $\tan \theta = \sin \theta / \cos \theta$
10. $\sin (\alpha \pm \beta) = \sin \alpha \cos \beta \pm \cos \alpha \sin \beta$
11. $\cos (\alpha \pm \beta) = \cos \alpha \cos \beta \mp \sin \alpha \sin \beta$
12. $\tan (\alpha \pm \beta) = \frac{\tan \alpha \pm \tan \beta}{1 \mp \tan \alpha \tan \beta}$
13. $\sin 2\theta = 2 \sin \theta \cos \theta$
14. $\cos 2\theta = \cos^2 \theta - \sin^2 \theta = 2 \cos^2 \theta - 1 = 1 - 2 \sin^2 \theta$
15. $\sin \alpha + \sin \beta = 2 \sin \frac{1}{2}(\alpha + \beta) \cos \frac{1}{2}(\alpha - \beta)$
16. $\cos \alpha + \cos \beta = 2 \cos \frac{1}{2}(\alpha + \beta) \cos \frac{1}{2}(\alpha - \beta)$

Triangles

1. Law of sines: $\frac{a}{\sin \alpha} = \frac{b}{\sin \beta} = \frac{c}{\sin \gamma}$
2. Law of cosines: $c^2 = a^2 + b^2 - 2ab \cos \gamma$



3. Pythagorean theorem: $a^2 + b^2 = c^2$



Series expansions

1. Binomial theorem:

$$(a + b)^n = a^n + na^{n-1}b + \frac{n(n-1)a^{n-2}b^2}{2!} + \frac{n(n-1)(n-2)a^{n-3}b^3}{3!} + \dots$$

$$2. (1 \pm x)^n = 1 \pm \frac{nx}{1!} + \frac{n(n-1)x^2}{2!} \pm \dots (x^2 < 1)$$

$$3. (1 \pm x)^{-n} = 1 \mp \frac{nx}{1!} + \frac{n(n+1)x^2}{2!} \mp \dots (x^2 < 1)$$

$$4. \sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \dots$$

$$5. \cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \dots$$

$$6. \tan x = x + \frac{x^3}{3} + \frac{2x^5}{15} + \dots$$

$$7. e^x = 1 + x + \frac{x^2}{2!} + \dots$$

$$8. \ln(1 + x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 - \dots (|x| < 1)$$

Derivatives

$$1. \frac{d}{dx} [af(x)] = a \frac{d}{dx} f(x)$$

$$2. \frac{d}{dx} [f(x) + g(x)] = \frac{d}{dx} f(x) + \frac{d}{dx} g(x)$$

$$3. \frac{d}{dx} [f(x)g(x)] = f(x) \frac{d}{dx} g(x) + g(x) \frac{d}{dx} f(x)$$

$$4. \frac{d}{dx} f(u) = \left[\frac{d}{du} f(u) \right] \frac{du}{dx}$$

$$5. \frac{d}{dx} x^m = mx^{m-1}$$

$$6. \frac{d}{dx} \sin x = \cos x$$

7. $\frac{d}{dx} \cos x = -\sin x$
8. $\frac{d}{dx} \tan x = \sec^2 x$
9. $\frac{d}{dx} \cot x = -\csc^2 x$
10. $\frac{d}{dx} \sec x = \tan x \sec x$
11. $\frac{d}{dx} \csc x = -\cot x \csc x$
12. $\frac{d}{dx} e^x = e^x$
13. $\frac{d}{dx} \ln x = \frac{1}{x}$
14. $\frac{d}{dx} \sin^{-1} x = \frac{1}{\sqrt{1-x^2}}$
15. $\frac{d}{dx} \cos^{-1} x = -\frac{1}{\sqrt{1-x^2}}$
16. $\frac{d}{dx} \tan^{-1} x = \frac{1}{1+x^2}$

Integrals

1. $\int a f(x) dx = a \int f(x) dx$
2. $\int [f(x) + g(x)] dx = \int f(x) dx + \int g(x) dx$
3. $\int x^m dx = \frac{x^{m+1}}{m+1} \quad (m \neq -1)$
 $\quad \quad \quad = \ln x \quad (m = -1)$
4. $\int \sin x \, dx = -\cos x$
5. $\int \cos x \, dx = \sin x$
6. $\int \tan x \, dx = \ln |\sec x|$
7. $\int \sin^2 ax \, dx = \frac{x}{2} - \frac{\sin 2ax}{4a}$
8. $\int \cos^2 ax \, dx = \frac{x}{2} + \frac{\sin 2ax}{4a}$
9. $\int \sin ax \cos ax \, dx = -\frac{\cos 2ax}{4a}$

$$10. \int e^{ax} dx = \frac{1}{a} e^{ax}$$

$$11. \int x e^{ax} dx = \frac{e^{ax}}{a^2} (ax - 1)$$

$$12. \int \ln ax dx = x \ln ax - x$$

$$13. \int \frac{dx}{a^2 + x^2} = \frac{1}{a} \tan^{-1} \frac{x}{a}$$

$$14. \int \frac{dx}{a^2 - x^2} = \frac{1}{2a} \ln \left| \frac{x+a}{x-a} \right|$$

$$15. \int \frac{dx}{\sqrt{a^2 + x^2}} = \sinh^{-1} \frac{x}{a}$$

$$16. \int \frac{dx}{\sqrt{a^2 - x^2}} = \sin^{-1} \frac{x}{a}$$

$$17. \int \sqrt{a^2 + x^2} dx = \frac{x}{2} \sqrt{a^2 + x^2} + \frac{a^2}{2} \sinh^{-1} \frac{x}{a}$$

$$18. \int \sqrt{a^2 - x^2} dx = \frac{x}{2} \sqrt{a^2 - x^2} + \frac{a^2}{2} \sin^{-1} \frac{x}{a}$$

Chemistry

Periodic Table of the Elements

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008 hydrogen																	2 He 4.003 helium
2	3 Li 6.94 lithium	4 Be 9.012 beryllium											5 B 10.81 boron	6 C 12.01 carbon	7 N 14.01 nitrogen	8 O 16.00 oxygen	9 F 19.00 fluorine	10 Ne 20.18 neon
3	11 Na 22.99 sodium	12 Mg 24.31 magnesium											13 Al 26.98 aluminum	14 Si 28.09 silicon	15 P 30.97 phosphorus	16 S 32.06 sulfur	17 Cl 35.45 chlorine	18 Ar 39.95 argon
4	19 K 39.10 potassium	20 Ca 40.08 calcium	21 Sc 44.96 scandium	22 Ti 47.87 titanium	23 V 50.94 vanadium	24 Cr 52.00 chromium	25 Mn 54.94 manganese	26 Fe 55.85 iron	27 Co 58.93 cobalt	28 Ni 58.69 nickel	29 Cu 63.55 copper	30 Zn 65.38 zinc	31 Ga 69.72 gallium	32 Ge 72.63 germanium	33 As 74.92 arsenic	34 Se 78.97 selenium	35 Br 79.90 bromine	36 Kr 83.80 krypton
5	37 Rb 85.47 rubidium	38 Sr 87.62 strontium	39 Y 88.91 yttrium	40 Zr 91.22 zirconium	41 Nb 92.91 niobium	42 Mo 95.95 molybdenum	43 Tc [97] technetium	44 Ru 101.1 ruthenium	45 Rh 102.9 rhodium	46 Pd 106.4 palladium	47 Ag 107.9 silver	48 Cd 112.4 cadmium	49 In 114.8 indium	50 Sn 118.7 tin	51 Sb 121.8 antimony	52 Te 127.6 tellurium	53 I 126.9 iodine	54 Xe 131.3 xenon
6	55 Cs 132.9 cesium	56 Ba 137.3 barium	57-71 La-Lu *	72 Hf 178.5 hafnium	73 Ta 180.9 tantalum	74 W 183.8 tungsten	75 Re 186.2 rhenium	76 Os 190.2 osmium	77 Ir 192.2 iridium	78 Pt 195.1 platinum	79 Au 197.0 gold	80 Hg 200.6 mercury	81 Tl 204.4 thallium	82 Pb 207.2 lead	83 Bi 209.0 bismuth	84 Po [209] polonium	85 At [210] astatine	86 Rn [222] radon
7	87 Fr [223] francium	88 Ra [226] radium	89-103 Ac-Lr **	104 Rf [267] rutherfordium	105 Db [270] dubnium	106 Sg [271] seaborgium	107 Bh [270] bohrium	108 Hs [277] hassium	109 Mt [276] meitnerium	110 Ds [281] darmstadtium	111 Rg [282] roentgenium	112 Cn [285] copernicium	113 Uut [285] ununtrium	114 Fl [289] flerovium	115 Uup [288] ununpentium	116 Lv [293] livermorium	117 Uus [294] ununseptium	118 Uuo [294] ununoctium
				57 La 138.9 lanthanum	58 Ce 140.1 cerium	59 Pr 140.9 praseodymium	60 Nd 144.2 neodymium	61 Pm [145] promethium	62 Sm 150.4 samarium	63 Eu 152.0 europium	64 Gd 157.3 gadolinium	65 Tb 158.9 terbium	66 Dy 162.5 dysprosium	67 Ho 164.9 holmium	68 Er 167.3 erbium	69 Tm 168.9 thulium	70 Yb 173.1 ytterbium	71 Lu 175.0 lutetium
				89 Ac [227] actinium	90 Th 232.0 thorium	91 Pa 231.0 protactinium	92 U 238.0 uranium	93 Np [237] neptunium	94 Pu [244] plutonium	95 Am [243] americium	96 Cm [247] curium	97 Bk [247] berkelium	98 Cf [251] californium	99 Es [252] einsteinium	100 Fm [257] fermium	101 Md [258] mendelevium	102 No [259] nobelium	103 Lr [262] lawrencium

Atomic number → 1

Symbol → H

Atomic mass → 1.008

Name → hydrogen

Color Code	
	Metal
	Metalloid
	Nonmetal
	Solid
	Liquid
	Gas

The Greek Alphabet

Name	Capital	Lowercase	Name	Capital	Lowercase
Alpha	A	α	Nu	N	ν
Beta	B	β	Xi	Ξ	ξ
Gamma	Γ	γ	Omicron	O	o
Delta	Δ	δ	Pi	Π	π
Epsilon	E	ϵ	Rho	P	ρ
Zeta	Z	ζ	Sigma	Σ	σ
Eta	H	η	Tau	T	τ
Theta	Θ	θ	Upsilon	Υ	υ
Iota	I	ι	Phi	Φ	ϕ
Kappa	K	κ	Chi	X	χ
Lambda	Λ	λ	Psi	ψ	ψ
Mu	M	μ	Omega	Ω	ω

The Greek Alphabet